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PROCEEDINGS

OF THE

CHEMICAL SECTION

OF THE

FRANKLIN INSTITUTE.

(VOL. II.—JAN.–DEC., 1890)

PHILADELPHIA:

1891.

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INDEX.

Vol. II, 1890.

Acid, fumaric, synthesis of. (Keiser), 23
Acid, lapachic, on some derivatives of. (Hooker and Greene), 112
Acid, lapachic, on some derivatives of. (Hooker), 112
Acid, picric, note on the compound of pyrrol with. (Hooker), 125
Alloys of sodium and lead. (Greene and Wahl), 84
Amines, metallic, the action of hydrogen sulphide gas on. (Smith and Keller), 85
Ammonia: on some constants of. (v. Strombeck), 90

CHEMICAL SECTION:
  Annual report for the year 1890, 127
  By-laws and list of members, v–x
  Proceedings. January to December, 1890, 1, 2, 22, 27, 37, 38, 67, 68, 82, 111, 127
Chlorine, action of, on hæmatoxylin and on the extractive matter of logwood. (MacFarlane and Clarkson), 14
Clarkson (Philip S.) and MacFarlane (Wm. W.). The action of chlorine on hæmatoxylin and on the extractive matter of logwood, 14

Electro-deposition of platinum. (Wahl), 39
Electrolytic method as applied to palladium. (Smith and Keller), 63
Electrolytic separations. (Smith and Frankel), 3

Frankel (L. K.) and Smith (E. F.). Electrolytic separations, 3
Fumaric acid, synthesis of. (Keiser), 23

Galvanized iron, on the use of, for artesian wells and for the conveyance of drinking water. (Haines), 69
Greene (Wm. H.) and Hooker (S. C.). On some derivatives of lapachic acid, 112
  Wahl (Wm. H.). Alloys of sodium and lead, 84

42085

Hæmatoxylin and the extractive matter of logwood, action of chlorine on. (MacFarlane and Clarkson), 14
Haines (Reuben). On the use of galvanized iron for artesian wells and for the conveyance of drinking water, 69
Himes (Chas. F.). A new photographic process without metallic salts (abstract), 88
Hooker (S. C.). Note on the compound of pyrrol with picric acid, 125
  On some derivatives of lapachic acid, 117
  On the present condition of the Philadelphia water supply, 28
  and Greene (Wm. H.). On some derivatives of lapachic acid, 112
Hydrogen sulphide gas, the action of, on metallic amines. (Smith and Keller), 85

Keiser (E. H). On the synthesis of fumaric acid, 23
Keller (H. F.) and Smith (E. F.). The electrolytic method as applied to palladium, 63
  The action of hydrogen sulphide gas upon metallic amines, 85

Lapachic acid, on some derivatives of. (Hooker), 112
Lapachic acid, on some derivatives of. (Hooker and Greene), 112
Logwood, extractive matter of, and hæmatoxylin, action of chlorine on. (MacFarlane and Clarkson), 14

MacFarlane (Wm. W.) and Clarkson (Philip S.). The action of chlorine on hæmatoxylin and on the extractive matter of logwood, 14

Oxidation of sulphides by means of the electric current. (Smith), 53
Ozokerite, Utah. (Seal), 78

Palladium, the electrolytic method as applied to. (Smith and Keller), 63
Photographic process, new, without metallic salts (abstract), 88
Picric acid, note on the compound of pyrrol with. (Hooker), 125
Platinum, electro-deposition of. (Wahl,) 39
Primuline printing, a new photographic process without metallic salts (abstract), 88
Pyrrol, note on the compound of, with picric acid. (Hooker), 125

Seal (Alfred N.). Utah ozokerite, 78
Smith (E. F.). The oxidation of sulphides by means of the electric current, 53
  and Frankel (L. K.). Electrolytic separations, 3
  and Keller (H. F.). The electrolytic method as applied to palladium, 63
  The action of hydrogen sulphide gas on metallic amines, 85
Strombeck (Hans v.). On some constants of ammonia, 90
Sulphides, oxidation of, by means of the electric current. (Smith), 53
Synthesis of fumaric acid. (Keiser), 23

Utah ozokerite. (Seal), 78

Wahl (Wm. H.). On the electro-deposition of platinum, 39
  and Greene (Wm. H.). Alloys of sodium and lead, 84
Water supply, Philadelphia, present condition of. (Hooker), 28

By-Laws

of the

Chemical Section

of the

Franklin Institute.

I. In accordance with article xi, section 4, of the by-laws of the institute, only members of the institute may be elected to membership in the section; but sections are empowered to appoint associates, corresponding members and honorary members, *provided* that such appointments are sanctioned by the board of managers. Associates shall have the privilege of attending the meetings of the section and of participating in its scientific discussions, but shall not be entitled to vote. They shall be required to pay an annual assessment of two dollars ($2), payable in accordance with article iii.

II. The committee on admissions shall consist of seven members. They shall be elected annually. Four members shall constitute a quorum at all meetings of this committee. The adverse vote of two members shall be a rejection of a candidate. Applications for admission to the section shall be in writing and signed by one member of the section. They shall be referred to this committee, after having been read before the section at a stated meeting. It shall be the duty of the committee, after careful consideration of the fitness of candidates, to vote on each name separately by ballot. This proceeding shall be secret and confidential. The committee shall send to the secretary of the section the names and addresses of the candidates elected. The committee shall have power to make its own rules of procedure.

III. Every member shall pay an initiation fee of one dollar ($1), and an annual contribution of two dollars ($2) in advance; but those elected to membership after October 1st shall pay no yearly dues for that year.

IV. Candidates elected to the section shall become members on payment of the initiation fee. If this fee is not paid within six months, the candidate's election shall be considered void. If the annual dues are not paid for a period of two years, due notice shall be given the member, and his name shall be stricken from the list.

V. The chemical apparatus, chemicals and other preparations belonging to the section, shall be under the care of the conservator, whose duty it shall be to see that they are kept in order and, if needed, readily accessible at the meetings of the section. He shall also attend to any minor repairs that may be necessary, and shall make an annual report to the section.

VI. The apparatus, reagents, etc., shall not be removed from the Franklin Institute building without consent of the conservator.

VII. A standing committee of two members shall be appointed yearly, who, with the secretary, shall be empowered to transact all financial business of the section, outside of the matters embraced in the duty of the treasurer. They shall pass all bills and shall audit the treasurer's account at the end of every year.

VIII. The stated meetings of the section shall be held on the third Tuesday of each month, except during July and August. Special meetings may be called by the secretary, at any time, on application of seven members.

IX. At the stated meeting in November, nominations shall be made, and at that in December, an election shall take place, for the following officers for the ensuing year:

President,
Two vice-presidents,
Secretary,
Treasurer,
Conservator.

The annual reports of the standing committees and officers shall be read at the December meeting.

X. The order of business for stated meetings shall be as follows:

(1) Correction of minutes of previous meeting.
(2) Nominations for membership.
(3) Report of committee on admissions.
(4) Reports of officers and correspondence.
(5) Reports of standing committees.
(6) Reports of special committees.
(7) Deferred business.
(8) New business.
(9) Communications and discussions.

XI. A quorum for the transaction of business shall consist of seven members.

XII. These by-laws may be temporarily suspended at any meeting of the section by unanimous consent of the members present. Amendments of a more permanent character may be made at any stated meeting by a vote of two-thirds of the members present; *provided*, that such amendments shall have been presented in writing and read before the section at a previous stated meeting.

Chemical Section.

Officers—1890.

President,	Mr. T. C. Palmer.
Vice-presidents,	Dr. H. F. Keller. Mr. W. L. Rowland.
Secretary,	Prof. Wm. C. Day.
Treasurer,	Dr. H. W. Jayne.
Conservator,	Dr. Wm. H. Wahl

LIST OF MEMBERS.

A.

A. W. Allen,	Pencoyd Iron Works, Pencoyd Pa.

B.

Henry Bower,	28th and Gray's Ferry Road.
W. H. Bower,	28th and Gray's Ferry Road.
Chas. H. Boyer,	528 Linden Street, Camden, N. J.
G. Genge Browning,	44 North Front Street.
Chas. Bullock,	528 Arch Street.
Wm. W. Bullock,	528 Arch Street.

C.

John E. Carter,	Coulter and Knox Streets, Germantown.
Prof. R. L. Chase,	1336 Spring Garden Street.
Dr. C. M. Cresson,	413 Locust Street.
Philip S. Clarkson,	Quaker City Dye Works, 110 Oxford St.
J. H. Campbell,	Kingman, Mojave County, Arizona.

D.

Prof. W. C. Day,	Swarthmore College, Pa.

E.

J. H. Eastwick,	Wissahickon Station.
A. T. Eastwick,	Isaac McHose & Sons, Norristown.

F.

R. A. Fisher,	2239 St. Alban's Place.

Lee K. Frankel, ... University of Pennsylvania.
Dr. Persifor Frazer, ... 1042, Drexel Building.

G.

Dr. Wm. H. Greene, ... 204 North 36th Street.
Hugh A. Galt, ... Kalion Chemical Company, 32d and Gray's Ferry Road.

H.

Dr. S. C. Hooker, ... Franklin Sugar Refinery.
Reuben Haines, ... 201 South 5th Street.
Prof. L. B. Hall, ... Haverford College.
Thos. G. Hunter, ... 55th and Paschall Ave.

I.

Fred. E. Ives, ... Crosscup & West, 9th and Filbert Sts.

J.

E. C. Jayne, ... 242 Chestnut Street.
H. W. Jayne, ... 931 North Broad Street.

K.

Dr. H. H. Keller, ... University of Pennsylvania.
Dr. Geo. A. Koenig, ... University of Pennsylvania.
Dr. E. H. Keiser, ... Bryn Mawr College.

L.

Dr. Otto Lüthy, ... 2336 Fairmount Avenue.
M. Carey Lea, ... 430 Walnut Street.
F. C. Lewin, ... 1011 Spruce Street.
John T. Lewis, ... 242 South 13th Street.

M.

L. J. Matos, ... 3943 Fairmount Avenue.
Prof. Henry Morton, ... Stevens Institute of Technology, Hoboken.
Wm. W. McFarlane, ... J. M. Sharpless & Co., Chester, Pa.
Dr. Alex. Muckle, ... 1323 North 19th Street.
Dr. L. I. Morris, ... 2505 Oxford Street.
A. A. Moore, ... Franklin Sugar Refinery.

N.

Thos. N. Newbold, ... 608 South 42d Street.
Geo. M. Newhall, ... 136 South 4th Street.
Geo. L. Norris, ... Pencoyd, Pa.

O.

Dr. E. L. Oatley, ... 4003 Chestnut Street.

P.

T. C. Palmer, ... 22 North Front Street.

H. Pemberton, ... 1947 Locust Street.
H. Pemberton, Jr., ... 1947 Locust Street.
C. V. Petræus, ... 231 South Front Street.
Geo. B. Phillips, ... 622 Race Street.

R.

W. L. Rowland, ... 4800 Chester Avenue.
Theo. D. Rand, ... 17 South 3d Street.

S.

Dr. Chas. Schaffer, ... 1309 Arch Street.
C. J. Semper, ... 505 South 41st Street.
Prof. S. P. Sadtler, ... 204 North 34th Street.
Prof. Edg. F. Smith, ... University of Pennsylvania.
H. G. Shaw, ... Kalion Chemical Company, 32d and Gray's Ferry Road.
Hermann Schanche, ... Harrison Bros. & Co., 36th and Gray's Ferry Road.
Pedro G. Salom, ... 926, Drexel Building.
Edward Stevens, ... 42d and Locust Streets.

T.

Prof. H. Trimble, ... 632 Marshall Street.
Prof. N. Wiley Thomas, ... Girard College.
Dr. D. K. Tuttle, ... U. S. Mint, Philadelphia.

W.

Asa W. Whitney, ... 1815 Vine Street.
Henry Warden, ... 18th and Alleghany Avenue.
Geo. C. Webster, ... Media, Pa.
Dr. Wm. H Wahl, ... Franklin Institute.
W. D. Weikel, ... Merchantsville, Camden County, N. J.
F. H. Wyeth, ... 11th and Washington Avenue.
Dr. T. R. Wolf, ... Newark, Del.
S. Lloyd Wiegand, ... 146 South 6th Street.
Lucius E. Williams, ... Swarthmore College.
Cabell Whitehead, ... Mint Bureau, Washington, D. C.

PROCEEDINGS

OF THE

CHEMICAL SECTION,

OF THE

FRANKLIN INSTITUTE.

[*Stated Meeting, held at the* INSTITUTE, *Tuesday, Jan. 21, 1890.*]

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, January 21, 1890.

Mr. T. C. PALMER, President, in the Chair.

Members present: Dr. L. B. Hall, Prof. E. F. Smith, Mr. Lee K. Frankel, Mr. W. W. Macfarlane, Mr. Philip S. Clarkson, Prof. E. H. Keiser, Dr. H. W. Jayne, Mr. A. W. Allen, Prof. N. Wiley Thomas, Mr. A. W. Whitney, Mr. L. J. Matos, Mr. G. L Norris, Dr. L. I. Morris, Mr. W. H. Bower, Mr. L. E. Williams, Mr. A. T. Eastwick, Mr. J. H. Eastwick, Mr. Reuben Haines, Dr. Wm. C. Day, and two visitors.

The President called the attention of the Section to By-Law II, relating to the election of a Committee on Admissions.

On motion, it was voted that the present Committee on Admissions be continued for the current year.

The President then appointed Messrs. A. T. Eastwick and L. J. Matos members of the Finance Committee for the ensuing year, as required by By-Law VII.

The Treasurer reported that the subscriptions for the journals taken by the Section had been arranged for, and that the cost was somewhat less for the present than for the past year.

The resignation of Mr. Jacob Lychenheim was read and accepted by vote of the Section.

Messrs. W. W. Macfarlane and Philip S. Clarkson presented a paper on "The Action of Chlorine or Hæmatoxylin and the Extractive Matter of Logwood." It was referred for publication in the JOURNAL OF THE INSTITUTE, and in the *American Chemical Journal.*

A discussion of the paper by the President and the authors of the paper followed.

Mr. Lee K. Frankel exhibited a specimen of crystallized silver deposited on a platinum dish by electrolysis from a solution of nitrate; the current employed was very weak. The specimen was examined with much interest by the members.

Adjourned.

WM. C. DAY, *Secretary.*

PROCEEDINGS.

[*Stated Meeting, held at the* INSTITUTE, *Tuesday, Feb. 18, 1890.*]

HALL OF THE FRANKLIN INSTITUTE.
PHILADELPHIA, February 18, 1890.

Mr. T. C. PALMER, President, in the Chair.

Members present: Profs. Sadtler, Smith, Trimble, Drs. Hooker, Keiser, Keller, Wahl, Messrs. Rowland, Macfarlane, Palmer, W. H. Bowers, Williams, Frankel, Galt, Jayne and four visitors.

Mr. Edw. K. Stevens, Forty-second and Locust Streets, was nominated for membership.

The resignation of H. N. Rittenhouse was presented, and on motion accepted.

Dr. E. H. Keiser presented a paper "On the Synthesis of Fumaric Acid," which was referred for publication in the JOURNAL.

Prof. E. F. Smith presented a paper on the electrolytic method as applied to palladium. (Referred for publication.) After the reading of the paper Prof. Smith exhibited six platinum dishes, containing, respectively, depositions of palladium, silver, nickel, cadmium, mercury and iron, obtained by the electrolytic methods described by him in this and former papers.

Dr Hooker spoke of the compound obtained from pyrrol by picric acid. On heating a mixture of equal molecules of the two at 58° to 60° until the picric acid is dissolved and cooling rapidly, long red needles crystallize out, which were rapidly dried by pressure between filter paper. If the mixture be heated above 60° the compound is not obtained. The method of analysis employed consisted in exposing a weighed quantity to the air and weighing again. This was repeated until weight became constant. The loss represented the pyrrol evaporated. The residue showed the melting-point of picric acid. Theory required 22·6 per cent. pyrrol for a compound of equal molecules of picric acid and pyrrol. Obtained 22·6, 22·7 and 22·9 per cent. loss.

Dr. Keller then presented a paper on Symmetrical Tetrabromacetyl, which was referred for publication.

At the conclusion of the meeting, the election of Mr. Edw. Stevens, as a member of the Section, was announced.

The meeting then adjourned. H. W. JAYNE, *Secretary pro tem.*

ELECTROLYTIC SEPARATIONS.

BY EDGAR F. SMITH AND LEE K. FRANKEL.

[*Read at the Stated Meeting of the Chemical Section, held December 17, 1889.*]

The study of the electrolysis of the double cyanides of cadmium, copper and zinc, enabled us to formulate conditions, by which the separations of cadmium from zinc (*American Chemical Journal*, **11,** 352,) and cadmium from copper (*Journal of Analytical Chemistry*, **3**, 385,) were possible, and in every particular satisfactory.

The ease with which cadmium was separated from zinc, and the very close results obtained with these metals, led us to apply the method to the separation of cadmium from cobalt and from nickel. Operating first with cadmium alone, we dissolved sufficient pure sulphate in water, so that 10 cc. of the solution would contain 0·1688 gram metallic cadmium. To this volume (10 cc.) were added four and one-half grams pure potassium cyanide, and the solution made up to 200 cc. with water. A current yielding 0·4 cc. O-H gas per minute, was allowed to act upon the same for a period of fourteen hours. The deposited metal weighed 0·1686 gram, a difference of —0·11 per cent. from the theoretical. A second trial, with conditions precisely analogous to those just mentioned, gave 0·1690 gram cadmium, a difference of + 0·11 per cent. from the theoretical.

CADMIUM FROM COBALT.

In the third experiment the conditions were the same as before, with this difference, that an equal amount of cobalt was also present in the solution. The result of the electrolysis was 0·1689 gram cadmium, a difference of + 0·05 per cent. from the required.

The fourth experiment, similar in every way to the third yielded 0·1689 gram cadmium, a difference of + 0·05 per cent. from the theoretical.

The cadmium was fully deposited on both occasions, and contained no cobalt.

CADMIUM FROM NICKEL.

Passing to the separation of cadmium from nickel, the results were so surprising, that we give the same in detail, although negative in character.

	Cadmium present in grams.	Nickel present.	Potassium Cyanide in grams.	Total dilution.	Strength of current in cc. O-H gas per minute.	Cadmium found.
1	0·1688	100 %	4½	200 cc.	0·3 cc.	0·1717
2	"	"	"	"	"	0·1702
3	"	"	"	"	"	0·1725
4	"	"	"	"	"	0·1750
5	"	"	"	"	"	0·1721
6	"	"	"	"	"	0·1737
7	0·1828	—	"	"	0·5 cc.	0·1827
8	"	75 %	"	"	"	0·1923
9	"	50 %	"	"	0·15 cc.	0·1841
10	"	"	"	"	0·5 cc.	0·1882
11	"	25 %	"	"	0·15 cc.	0·1854

The period of time during which the current acted in each of the above experiments was sixteen hours. Nickel was always found in the cadmium deposit, while in many cases the precipitation of the cadmium was incomplete. The conditions were varied, yet the results were wholly unsatisfactory. By greatly increasing the quantity of cyanide, we discovered that the cadmium precipitation was retarded. Nickel when alone, and when under the conditions given above, would not deposit with the strength of current used by us. This behavior is only another indication, that if we would make electrolytic methods widely applicable, it is first necessary to extend the study of the action of the current to all the salts possible, and to investigate carefully the influence of each metal upon its associates under varying conditions.

From what we have thus far accomplished, we find the electrolytic separation of cadmium from copper, from zinc, and from cobalt, in cyanide solution, all that could be expected from any method. The cadmium deposits, in the experiments recorded in this paper, were always washed with boiling water; the drying was done upon the edge of a warm iron plate.

We have already called attention (*American Chemical Journal*, **11**, 264,) to the fact that mercury is fully precipitated from the solution of its double cyanide by a comparatively feeble current, and that the separation of this metal from copper is possible, so long as the quantity of the latter does not exceed twenty per cent. of the mercury present.

More recently we have executed a series of experiments looking to the separation of mercury from zinc, nickel and cobalt.

MERCURY FROM ZINC.

The results with these metals are:

	Mercury present in grams.	Zinc present.	KCN in grams.	Total dilution.	Current strength in cc. O-H gas per minute.	Mercury found.	Difference in % from theoretical.
1	0·1715	—	4½	200 cc.	0·3 cc.	0·1717	+ 0·12 %
2	"	—	"	"	"	0·1715	—
3	"	100 %	"	"	0·25 cc.	0·1706	— 0·52 %
4	"	"	"	"	"	0·1709	— 0·34 %

The time in each deposition was sixteen hours. From these figures the separation is possible. Mercury was not found with the zinc. In the following experiments it will be observed that the error is much less, and accordingly makes the method trustworthy, and from its accuracy, well-suited for scientific as well as technical work:

	Mercury present in grams.	Zinc present.	KCN in grams.	Total dilution.	Current strength in cc. O-H gas per minute.	Mercury found.	Difference in % from the theoretical.
5	0·2440	100 %	3	200 cc.	0·5 cc.	0·2435	— 0·20 %
6	"	"	3	"	"	0·2445	+ 0·20 %
7	"	"	4½	"	"	0·2441	+ 0·04 %
8	"	"	"	"	0·28 cc.	0·2445	+ 0·20 %
9	"	"	"	"	"	0·2431	+ 0·37 %
10	"	"	"	"	"	0·2454	+ 0·50 %

The time of precipitation, made at the ordinary temperature, amounted to sixteen hours. The mercury deposit was washed with hot water, and dried upon a moderately warm iron plate.

MERCURY FROM NICKEL.

With these two metals the current was allowed to act for sixteen hours. The results are as follows:

	Mercury present in grams.	Nickel present.	KCN in grams.	Total dilution.	Current strength in cc. O-H gas per minute.	Mercury found.	Difference in % from the theoretical.
1	0·2440	100 %	4½	200 cc.	0·4 cc.	0·2435	— 0·20 %
2	"	"	"	"	"	0·2432	— 0·32 %
3	"	"	"	"	"	0·2425	— 0·60 %

MERCURY FROM COBALT.

Our experience with these two metals was so unexpected that we append the poor as well as the good results which were finally obtained:

	Mercury present in grams.	Cobalt present.	KCN in grams.	Total dilution.	Current in cc. O-H gas per minute.	Mercury found.	Difference in % from the theoretical.
1	0·2440	100 %	4½	200 cc.	0·4 cc.	0·2386	— 2 21 %
2	“	“	“	“	“	0·2388	— 2·13 %
3	“	“	“	“	“	0·2364	— 3·11 %
4	“	“	“	“	“	0·2333	— 4·00 %
5	“	“	“	“	“	0·2366	— 3 02 %

The current acted for sixteen hours, upon reducing the quantity of cobalt, and operating with the conditions, in other respects, the same as before (except in 11 and 13), we obtained:

	Mercury present in grams.	Cobalt present.	KCN in grams.	Total dilution.	Current in cc. O-H gas per minute.	Mercury found.	Difference in % from the theoretical.
6	0·2440	75 %	4½	200 cc.	0·5 cc.	0·2353	— 3·56 %
7	“	“	“	“	0·86 cc.	0·2357	— 3·40 %
8	“	50 %	“	“	0·5 cc.	0·2387	— 2·25 %
9	“	“	“	“	“	0·2381	— 2·33 %
10	“	“	“	“	0·86 cc.	0·2321	— 4·80 %
11	“	25 %	3	“	0·5 cc.	0·2442	+ 0·09 %
12	“	“	4½	“	0·86 cc.	0·2342	— 4·01 %
13	“	12½ %	3	“	0·5 cc.	0·2445	+ 0·20 %

Inspection of these figures discloses the fact that nothing approaching a separation of the two metals appears probable until in experiment (11), where not only the quantity of cobalt is reduced, but also that of the potassium cyanide. The result is then surprisingly close (+·09 per cent.). This would seem to be due rather to the reduction of the quantity of cyanide, inasmuch as by its increase in experiment (12), we again have a minus error of 4·01 per cent.

and in experiment (13), by reducing the quantity of cyanide to three grams, the result is satisfactory. As the quantity of cobalt, in this instance, was but half of that in experiment (12), the favorable result might be attributed to this. Hence, the following trials were made:

	Mercury present in grams.	Cobalt present.	KCN in grams.	Total dilution.	Current in cc. O-H gas per minute.	Mercury found.	Time of precipitation.	Difference in %.
14	0·2250	—	3	200 cc.	0·5 cc.	0·2250	16 hours.	—
15	"	25 %	"	"	"	0·2256	"	+ 0·26 %
16	"	50 %	"	"	"	0·2258	"	+ 0·35 %
17	"	75 %	"	"	"	0·2258	"	+ 0·35 %
18	"	100 %	2·2	"	"	0·2235	"	— 0·60 %

Cobalt was not found in the mercury deposit, nor mercury in the cobalt solution.

Evidently the quantity of cyanide present exercises a marked influence upon the separation. Returning to the separation of cadmium from cobalt, it will be observed that the amount of cyanide present there, was four and a half grams, while the quantity of metal was less, yet the separation proved satisfactory.

SILVER FROM COPPER.

It yet remains for us to record some experiments upon the separation of these two metals in cyanide solution. Reference to a former paper (*American Chemical Journal*, **11,** 264, and *Journal of Analytical Chemistry*, **3,** 254,) will show that our attempts in this direction were at that time fruitless. It was after the successful separation of cadmium from copper in cyanide solution that we were impressed with the idea that the separation of silver from copper ought to occur, since silver deposits so readily, even when exposed to a very feeble current. In the communication to which we refer, the current strength recorded was

1 cc. O-H gas per minute. Since it was, by carefully reducing this in other cases, that we obtained good separations, we instituted a new series of experiments with silver and copper, acting upon the mixture with a much weaker current:

	Silver present in grams.	Copper present.	KCN in grams.	Total dilution.	Current in cc. O-H gas per minute.	Time in hours.	Silver found.	Difference in %.
1	0·1788	—	4½	200 cc.	0·10 cc.	16	0·1792	+ 0·22 %
2	"	—	"	"	0·23 "	"	0·1788	—
3	"	100 %	"	"	0·15 "	"	0·1788	—
4	"	"	"	"	0·30 "	"	0·1787	— 0·05 %
5	"	"	"	"	0·20 "	"	0·1784	— 0·20 %
6	"	"	"	"	" "	"	0·1782	— 0·33 %
7	"	"	"	"	0·40 "	"	0·1783	— 0·28 %
8	"	"	"	"	0·15 "	"	0·1800	+ 0·60 %

We next dissolved 0·1732 gram pure metallic silver in nitric acid. To its solution, after evaporation, there were added 100 per cent. copper and four and a half grams potassium cyanide. On electrolyzing, with a current of 0·15 cc. O-H gas per minute, the resulting silver weighed 0·1725 gram. The latter contained no copper, nor could silver be detected in the copper solution.

A silver ten-cent piece, weighing 1·2236 grams, was brought into solution and diluted to 100 cc. Of this solution, two portions (25 cc. each) were electrolyzed in the presence of four and a half grams potassium cyanide, with a current of 0·4 cc. O-H gas per minute. The silver found was in:

(*a*) 89·64 per cent.
(*b*) 89·56 per cent.

Two silver determinations made with another coin gave:

(*c*) 89·44 per cent.
(*d*) 89·44 per cent.

A silver dime, weighing 2·4507 grams, carefully cleaned with sodium hydroxide and alcohol, after solution in nitric acid, and the expulsion of the excess of the latter, was electrolyzed with a current of 0·7 cc. O-H gas per minute, in the presence of seven grams potassium cyanide, and gave 2·1996 grams silver = 89·79 per cent.

So far as we are aware, this is the first electrolytic method, which has been proposed for the separation of these two metals.

SILVER FROM ZINC.

No difficulty is experienced in separating these metals when in cyanide solution. Our results are as follows:

	Silver present in grams.	Zinc present.	KCN in grams.	Total dilution.	Current in cc. O-H gas per minute.	Time in hours.	Silver found	Difference in %.
1	0·1788	100 %	4½	200 cc.	0·23 cc.	16	0·1784	— 0·22 %
2	"	"	"	"	0·40 cc.	"	0·1785	— 0·11 %
3	"	"	"	"	"	"	0·1779	— 0·50 %
4	"	"	"	"	"	"	0·1787	— 0·05 %

Applying the same procedure to the separation of

SILVER FROM NICKEL,

the results obtained were equally as good:

	Silver present in grams.	Nickel present.	KCN in grams.	Total dilution.	Current in cc. O-H gas per minute.	Time in hours.	Silver found.	Difference in %.
1	0·1788	100 %	4½	200 cc.	0·35 cc.	16	0·1785	— 0·16 %
2	"	"	"	"	"	"	0·1778	— 0·50

SILVER FROM COBALT.

The following are the results obtained:

	Silver present in grams.	Cobalt present.	KCN in grams.	Total dilution.	Strength of current in cc. O-H gas per minute.	Time in hours.	Silver found.
1	0·1788	100 %	4½	200 cc.	0·35 cc.	16	0·1728
2	"	"	"	"	"	"	0·1747
3	"	"	"	"	"	"	0·1758
4	"	"	"	"	"	"	0·1697

Recalling our experience in separating mercury from cobalt, we reduced the quantity of cyanide to three grams, and obtained:

	Silver present in grams.	Cobalt present.	KCN in grams.	Total dilution.	Current in cc. O.H gas per minute	Time in hours.	Silver found.	Difference in %.
5	0·1788	100 %	3	200 cc.	0·35 cc.	16	0·1794	+ 0·33%
6	"	"	"	"	"	"	0·1782	— 0·33%

From experiments made to learn the action of the current upon solutions of cobalt in the presence of a great excess of potassium cyanide, we know that the higher cyanide of cobalt—the cobalticyanide—is produced, and may it not be this, which in some manner combines with the last traces of mercury and silver to form double cyanides not decomposable by the current strength employed in our experiments, which, if increased, would throw out not only the mercury and silver, but also some cobalt?

With cadmium, the double compound, if formed, may be more readily broken up, hence the separation is easily made. By reducing the quantity of potassium cyanide with mercury and silver, we afford no opportunity for the production of cobalticyanide in such quantity as to appreciably affect the deposition of the other metals.

COPPER FROM CADMIUM IN THE PRESENCE OF SULPHURIC ACID.

From the fact that it is possible to precipitate cadmium completely from the solution of its sulphate, containing free sulphuric acid (Smith, *American Chemical Journal*, **2** 42), and as copper is also deposited under similar conditions, the separation of these metals, when in this form, would hardly be expected. The experiments given below, show that notwithstanding all this, their separation can be effected under the conditions indicated. The first results were negative:

Ten cc. copper sulphate (0·1975 gram metallic copper, 10 cc. cadmium sulphate (0·1828 gram metallic cadmium), 1 cc. H_2SO_4 (sp. gr. 1·09) with 150 cc. water were electrolyzed with a current generating 0·4 cc. O-H gas per minute. The copper was fully precipitated, and with it considerable cadmium.

In a second series of three experiments, similar to that above, excepting that the current only gave 0·22 cc. O-H gas per minute, the copper was entirely precipitated, but carried down some cadmium with it.

In a third series of three experiments, the sulphuric acid in each dish was increased to 5 cc. (sp. gr. 1·09). The current gave 0·22 cc. O-H gas per minute. The copper was not completely precipitated, and cadmium had deposited on the copper.

The fourth series was made up as follows:

(1) 10 cc. copper sulphate = 0·1975 gram copper.

10 cc. cadmium sulphate = 0·1828 gram cadmium.

10 cc. H_2SO_4 (sp. gr. 1·09.)

100 cc. water. Current = 0·3 cc. O-H gas per minute. Time, 12 hours. The copper deposit weighed 0·1968 gram.

(2) Same as (1), copper found = 0·1964 gram.

(3) 10 cc. cadmium sulphate = 0·1828 gram cadmium, 5 cc. H_2SO_4 (sp. gr. 1·09). 100 cc. water. Current as in (1) and (2). Cadmium was not precipitated.

In the fifth series of four experiments, a current generating 0·5 cc. O-H gas per minute was employed. The quantity of acid was increased to 10 cc. and 15 cc. cadmium separated together with the copper.

The sixth series included five experiments:

(1) 10 cc. copper sulphate = 0·1975 gram copper.
10 cc. cadmium sulphate = 0·1828 gram cadmium.
15 cc. H_2SO_4 (sp. gr. 1·09.)
100 cc. water. Current = 2 cc. O-H gas per minute.
Copper found = 0·1969 gram copper.

(2) Same as (1), gave 0·1976 gram copper.

(3) Same as (1) and (2), except that the current generated 0·3 cc. O-H gas per minute. Copper found = 0·1975 gram.

Experiments (4) and (5) were like (3). The copper deposited equalled 0·1969 gram and 0·1962 gram. Tabulating the results, we have:

	Copper required.	Copper found.	Difference in %.
1	0·1975	0·1968	—0·35
2	"	0·1964	—0·55
3	"	0·1969	—0·30
4	"	0·1976	+0·05
5	"	0·1975	—
6	"	0·1969	—0·30
7	"	0·1962	—0·65

The filtrates from the deposited copper were examined for that metal. (7) showed a trace of copper. Cadmium was not detected in the precipitated metal. Holding strictly to the conditions given above, will enable any one to effect the separation of these two metals in the presence of sulphuric acid.

UNIVERSITY OF PENNSYLVANIA,
January 6, 1890.

THE ACTION OF CHLORINE ON HÆMATOXYLIN AND THE EXTRACTIVE MATTER OF LOGWOOD.

By WM. W. MACFARLANE and PHILIP S. CLARKSON.

[*Read at the Stated Meeting of the Section, January 21, 1890.*]

It is well-known among dyers, who have had any experience in extracting the coloring matter from logwood by boiling the wood under pressure in closed vessels, that a larger quantity of wood, when so treated, is required for dyeing a given quantity of material, than when the coloring matter is extracted by boiling the wood in an open vessel, such as a dye tub. It was the desire to discover the cause of this difference, and to avoid the loss of coloring matter, that led to a long series of experiments, and the discovery that chlorine can be used to increase the dyeing power of the extractive matter of logwood, and also that hæmatoxylin and hæmatein have entirely different values for the dyer, depending upon the manner in which they are used; that is, whether used for coloring wool or cotton, and whether the dyeing is done in an acid, alkaline or neutral bath.

Logwood, before it is used by the dyer, is treated by a process called "curing," which consists in saturating the chipped or ground wood with water, then allowing it to lie in heaps or beds until a kind of fermentation or heating takes place. It is then necessary to move it frequently to avoid any considerable increase in temperature, and to expose all portions of it to the oxidizing influence of the air. Exactly what takes place in this curing process is not known, as the composition of the extractive matter of logwood has not been determined. It is known that the wood contains hæmatoxylin, and it is supposed that certain glucosides are present, which, during the process of curing, are broken up, yielding hæmatoxylin or hæmatein. Hæmatein is produced during this process, as will be shown later. Wood which has been subjected to this treatment, although it contains from ten to twenty-five per cent. more water, gives the dyer much better results, particularly on wool, than an equal weight of the wood in the condition it comes from the chipping or grinding machines.

For a long time attempts have been made to develop, or increase the dyeing power of the extractive matter of logwood, either during the extraction process, or after the extractive matter had been obtained in an aqueous solution. Most of the substances used for this purpose are oxidizing agents, and are used probably with the idea of converting hæmatoxylin into hæmatein. In 1885, C. E. Avery obtained a United States patent for the oxidizing of logwood liquors or extracts by the action of "oxidants such as a solution of bleaching powder, hypochlorous acid, chloric acid, chlorates or nitrates of the alkalies and alkaline earths." He further claims the use, for this purpose, of "oxidizing substances, such as solutions of chlorates of potash, or lime, or nitrates of potash, soda, or lime, which, whilst mixing with the logwood liquor at moderate temperatures, oxidize slowly or not at all, but on raising the temperature, particularly under pressure, or by the addition of acid or acid salts, become oxidizers of hæmatoxylin to hæmatein." In the specification of this patent, the quantity of a chlorate or nitrate necessary to convert a given quantity of hæmatoxylin is stated, but no directions are given as to the quantity of bleaching powder, or hypochlorous acid to be used to effect the desired result. The authors made many experiments, both following closely the specification of this patent, and with variation of the quantity of oxidants, and of the method of using them, but were not able to obtain any results which would pay for the labor and material used. In using a solution of bleaching powder for this purpose, it was assumed that the combined or available chlorine was the oxidizing agent intended to convert the hæmatoxylin to hæmatein, and although many experiments were tried the result was invariably a dull gray shade of black.

In Wurtz's *Dictionnaire de Chemie* (vol. i, pt. 1, p. 645,) it is stated that chlorine converts hæmatoxylin into a brown amorphous mass. Erdmann (*Jour. für Prak. Chemie*, **26**, 202), Reim (*Berichte der Deut. Chem. Gesell.*, 1871, p. 329,) and Dralle (*Ber. der D. Chem. Gesell.*, 1884, p. 372), found that no definite and separate compounds were formed by the action of chlorine on hæmatoxylin. After many fruitless experiments, and when all probable means of producing the desired result had been tried, it was determined to make some experiments, using free chlorine, added in the form of an aqueous solution, to the solution of the coloring matter. For this purpose a dilute aqueous solution of the extractive matter of cured wood was used. The results were determined by making dyeing tests in the mixed solutions with skeins of woollen yarn mordanted with potassium dichromate and potassium bitartrate. The results were surprising, and showed that the depth of color increased with the amount of chlorine used, until a maximum quantity was reached, when any further increase in the quantity of chlorine produced a dull and gray shade. After further experiments, it was found that by using a 42° extract of logwood, which had undoubtedly been made from dry cut wood; that is, wood not subjected to the curing process, and chlorine equivalent to about nine per cent. of the weight of the extract, the dyeing power of the coloring matter was increased 150 per cent.

Owing to the difficulties experienced in making and handling large quantities of chlorine water, it was found necessary to devise some other means of treating the extractive matter with the chlorine. Very good results were obtained by circulating the solution of the extractive matter through any suitable vessel, so arranged as to expose as large a surface of the solution as possible, and into this vessel the chlorine gas was delivered from the generator. The quantity of chlorine used was regulated by the quantity of materials placed in the generator. Later, it was found that if, during the absorption of the chlorine, the temperature of the solution was maintained at about 80° C., less chlorine was required to produce the desired result than when the action took place at the ordinary temperature.

It has been stated that by increasing the coloring power of the logwood by the use of oxidizing substances, the colors obtained are not fast on exposure to light and air. In practice, however, it was found that a sample of worsted cloth dyed black on chromium mordant with logwood extract developed with chlorine, after an exposure of six weeks, had not undergone any more change in shade than a sample dyed with ordinary cured wood.

In order to ascertain the exact chemical change which takes place in the hæmatoxylin in this process, a sample was obtained, manufactured by E. Moerk, and treated in the same manner as the extract. First, to determine the amount of chlorine necessary to yield the greatest dyeing power, samples were treated with varying amounts of chlorine and dye tests made. It was found that the greatest development was obtained when the proportion of chlorine was four atoms to each molecule of hæmatoxylin, which is equal to forty-seven per cent. of the hæmatoxylin. This would indicate a more complex reaction than the conversion of hæmatoxylin to hæmatein, as that would require but two atoms of chlorine for each molecule of hæmatoxylin.

$$C_{16}H_{14}O_6 + Cl_2 = C_{16}H_{12}O_6 + 2\,HCl$$

Avery, in his patent, calculates the amount of oxidizing agents necessary, on the basis of the simple reaction—

$$C_{16}H_{14}O_6 + O = H_2O + C_{16}H_{12}O_6$$

This constitutes a marked difference in the two processes. A larger quantity of chlorine renders the shade dull and gray.

It is stated by various authorities, especially by Dralle (*Berichte*, 1884, Feb., p. 372), that no separable compounds are obtainable by the action of chlorine on hæmatoxylin and that hæmatein is not formed in the reaction. An attempt was made to determine the products of this action and a larger quantity of hæmatoxylin was treated with the proportional amount of chlorine, viz: four atoms of chlorine to each molecule of hæmatoxylin. The method used was to dissolve the hæmatoxylin in hot water, allow it to cool and then treat with chlorine water containing the calculated amount of chlorine gas. By repeated washing with ether, containing a small portion of alcohol, and distilling off the ether and drying, there was left a brownish, resinous mass, completely soluble in alcohol. By treatment of this residue with chloroform, a white crystalline substance was separated. This was soluble in ether, water, chloroform and acetic acid. However, this was not obtained in sufficient quantity to determine the composition or characteristics. By farther treatment of this residue with ether, two bodies were separated; one with a brownish, resinous appearance, the other with a bright greenish, metallic lustre. By saturation of the original solution with common salt, and again treating with ether, more matter was extracted, but was found to consist mainly of brown, resinous matter. Since this method of saturating the solution with salt to separate the products of this reaction appears to have been used in former investigations, it is probably the cause of the statement that only resinous bodies, not admitting of purification, are the result of the action of chlorine on hæmatoxylin.

By carefully distilling the ether from the washing of the solution, it is possible to separate most of the bronze substance before the solution is completely evaporated. It then separates in shining scales, which are apparently not crystalline. These contain small amounts of the resinous matter. By washing with ether several times, it is possible to obtain a bright greenish bronze body, with a strong metallic lustre. This gives a red, almost approaching violet, powder. Although seemingly pure, it contains a trace of chlorine and has not been obtained sufficiently pure to warrant a determination of the composition by combustion. It is insoluble in cold water, somewhat more soluble in hot water, freely soluble in alcohol, almost insoluble in ether and chloroform. It has powerful dyeing properties, five per cent. on wool giving a blue black. Therefore, in its physical characteristics and chemical properties, it is identical with hæmatein, and justifies the supposition that it is hæmatein. It is hoped to obtain this in a state sufficiently pure to make a determination of the composition.

The resinous substance is easily soluble in ether, alcohol and water. It appears to be a chlorine substitution product of either hæmatein or hæmatoxylin, as the amount of chlorine contained in mixtures of this and hæmatein is in proportion to the amount of this substance. It remains in the dye bath, after the hæmatein has been absorbed by the wool, and probably has no effect on the color produced. The difficulty in completely separating these bodies lies in the fact that hæmatein is soluble in solutions containing the resinous matter; therefore, it is very difficult to obtain one entirely free from the other.

In order to have some standard of comparison with the coloring matter of logwood after curing, a well-bronzed sample of wood was treated with alcohol. To this solution, which was brownish-yellow, hydrochloric acid was added, and the whole distilled to a small volume. On cooling, there was an abundant separation of coloring matter which, after treatment with ether and alcohol, remained as a bronze powder. A combustion of this was made, which gave—

	Erdmann found
C, 62·94	62·66
H, 4·31	4·16
O, 32·75	33·18

From this it is evident that this is the same as the hæmatein obtained by Erdmann by the oxidation of hæmatoxylin in the presence of ammonia.

On making comparative dye tests of the coloring matter obtained by the action of chlorine on hæmatoxylin and this extracted from cured wood, the colors obtained were very similar in depth and shade; that of the hæmatein from wood being slightly duller. Both were about double the color obtained with hæmatoxylin. With the latter it is very doubtful if any deeper shade than a very light blue would be obtained if the air were entirely excluded from the bath; the shade constantly growing deeper in proportion to the time the dyeing is continued, while with hæmatein the bath is exhausted in a comparatively short time and no farther increase of color occurs.

In practical dyeing there are several methods in use which are radically different; wool dyeing being carried out in a neutral or slightly acid bath at 100° C.; cotton dyeing, commonly in a slightly alkaline solution, and what is known as speck-dyeing, in a strongly alkaline solution containing caustic alkali at a temperature below 15° C. Speck-dye is used to color the cotton in mixed goods after the wool has been dyed, or to color the burrs and other vegetable substances which may have become mixed with the wool. The low temperature is employed to prevent the wool absorbing any color during the operation. From the differing conditions, it was considered probable that varying results would be obtained from the use of the same coloring matter in each of these methods. In the experiment with wool, equal weights of woollen yarn were taken and mordanted with three per cent. potassium dichromate and two per cent. of potassium bitartrate. These skeins were then dyed with five per cent. each of hæmatoxylin, hæmatein from cured wood and hæmatein obtained with chlorine. The operation was carried on at a boil for one hour. The shade given by the two hæmateins was at least twice as full as that obtained from hæmatoxylin. Next some speck-dye was made of the same substances in the following proportions: five per cent. coloring matter, forty-four sodium carbonate, five sodium hydrate, one of sodium sulphite and sixteen of copper sulphate; each dissolved in water, the solutions mixed, made up to equal volumes, boiled and allowed to cool. The skeins of unmordanted cotton yarn of equal weights were then dyed in these baths. In this case the shade obtained with hæmatoxylin was much darker than with the hæmateins; these being of little practical value. There was a marked difference in the appearance of the baths, that of the hæmatoxylin being of a deep purple color, with little or no precipitate, the other two of a blue color, with much precipitate.

Noticing a yellowish color in this precipitate, which might have been due to the reduction of the copper, the action of each of these substances was tried on Fehling's solution. It was reduced by hæmatoxylin much more slowly than by hæmatein; but it was found that more copper was reduced by the hæmatoxylin than by the hæmatein. Fifty milligrammes of hæmatoxylin gave ·1675 gram Cu_2O, and the same quantity of hæmatein, ·1541 gram Cu_2O. These may not be the constant reduction proportions, as this was not tried under varying conditions; but these figures were obtained by treating the bodies with an excess of Fehling's solution. A farther report will be made on this subject. From these experiments it would appear that when alkaline solutions are used in the application of logwood, the extract or decoction should be made of dry cut wood, while for wool much better results are obtained by the use of cured wood.

On finding that free chlorine in proper proportions would increase the dyeing powers of logwood extract and that an excess produced dull and gray shades similar to those obtained by the use of bleaching powder or calcium hypochlorite, the experiment was tried of reducing the amount of the calcium salt to about half the theoretical quantity. When this was done, a marked increase of color was obtained, with no deterioration in shade. It has been shown that the greatest development of the dyeing power of hæmatoxylin results when forty-seven per cent. of free chlorine is used; but when a solution of bleaching powder is employed, the same effect is produced when the proportion of available chlorine to hæmatoxylin is but twenty-three and one-half per cent.

PHILADELPHIA, January 21, 1890.

PROCEEDINGS.

[*Stated Meeting, held at the* INSTITUTE, *Tuesday, March 18, 1890.*]

HALL OF THE FRANKLIN INSTITUTE.
PHILADELPHIA, March 18, 1890.

In the absence of the President and Vice-Presidents, Dr. L. B. HALL was elected by the Section President *pro tem.*

Members present: Dr. H. W. Jayne, C. J. Semper, H. Pemberton, Jr., L. E. Williams, J. H. Eastwick, Prof. N. Wiley Thomas, Dr. S. C. Hooker, Reuben Haines, A. W. Allen, L. J. Matos, Philip S. Clarkson, Dr. L. I. Morris.

A letter from Dr. Wahl was read, in which he called the attention of the Section to the fact that at his suggestion the Library Committee had authorized the purchase of the complete set of Liebig's *Annalen*, from 1832 to 1886. He also recommended that the Section subscribe for this journal regularly, commencing with 1887. On motion, the Section voted that the Treasurer be authorized to continue the subscription, as suggested by Dr. Wahl.

The Treasurer called the attention of the Section to the very satisfactory condition of the treasury, and recommended that expenditures for additional journals, as well as standard works of reference, be made. On motion, the Section voted that a committee be appointed by the Chair to make selections of such journals or other works as might be purchased, the committee to report to the Section at a future meeting. The President appointed J. H. Eastwick, Dr. H. W. Jayne, Dr. S. C. Hooker and Dr. Wm. H. Wahl, members of this committee.

Dr. Hooker called the attention of the Section to some new developments in the work conducted by himself and Dr. Greene on lapachic acid and its derivatives. Certain points of difference in the views of the authors on the one hand and E. Paterno, on the other, concerning the structure of these bodies, were made clear in his remarks, which were listened to with much interest by the members.

Mr. Reuben Haines called the attention of the Section to Dr. Pruden's recently published work on Bacteriology. He discoursed at some length various points of general interest in the work.

Dr. L. B. Hall referred to an observation recently made by him of the peculiar blue color which a mixture of sulphuric acid and phosphorous pentoxide assumes on standing for a time. The observation was made in connection with the application of Kjehldahl's method of determining nitrogen. None of the members present had ever noticed the phenomenon.

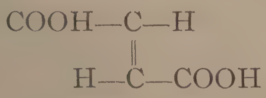
Adjourned. Wm. C. Day, *Secretary.*

ON THE SYNTHESIS OF FUMARIC ACID.

By E. H. Keiser.

[*Read at the Stated Meeting of the Chemical Section, held February 20, 1890.*]
[*Preliminary Communication.*]

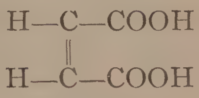
Van't Hoff * has proposed the following stereometric formulæ for fumaric and maleic acids:



$$\begin{array}{c}\text{COOH—C—H}\\ \| \\ \text{H—C—COOH}\end{array}$$

Fumaric acid.

and

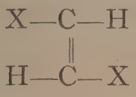


$$\begin{array}{c}\text{H—C—COOH}\\ \| \\ \text{H—C—COOH}\end{array}$$

Maleic acid.

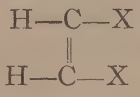
Johannes Wislicenus† has shown in a series of important papers that it is possible to determine experimentally the stereometric formulæ of certain isomeric compounds. A consideration of the hypothesis put forward by him suggested the idea that it ought to be possible to prepare both fumaric and maleic acids synthetically from acetylene. In accordance with Van't Hoff and Wislicenus' theory, the di-halogen additive compounds of acetylene can exist in two isomeric forms having the formulæ:

I.



$$\begin{array}{c}\text{X—C—H}\\ \| \\ \text{H—C—X}\end{array}$$

and II.



$$\begin{array}{c}\text{H—C—X}\\ \| \\ \text{H—C—X}\end{array}$$

in which X represents any halogen atom. And, further, compounds having the constitution represented by formula I are more stable than those having the structure represented by the second formula. Fumaric acid would then appear to be closely related to the halogen derivatives of the first class, and maleic acid to those of the second.

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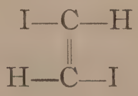
* *Lagerung der Atome im Raume*, p. 21.

† *Räumliche Anordnung der Atome in organischen Molekülen. Ann. Chem.* (Liebig), **246**, 53.

It occurred to me that it might, perhaps, be of interest in this connection to start with acetylene, and prepare, in the first place, two isomeric di-halogen additive compounds, and then endeavor to transform these into fumaric and maleic acid. The investigation is not yet completed, but one of the acids, namely, fumaric acid, has been prepared in this way from acetylene.

Acetylene was prepared by the action of alcoholic potash upon ethylene bromide, and the purified gas was passed through a series of wash-bottles containing crystals of iodine covered with a layer of absolute alcohol. After a time, the iodine disappeared, and from the liquid two isomeric acetylene di-iodides were separated. One of these compounds is a solid at ordinary temperatures; the other is a liquid. The solid di-iodide is much more stable than the liquid variety. It does not decompose on standing, and can be sublimed without suffering change. On the other hand, the liquid di-iodide undergoes decomposition when heated, and cannot be distilled with steam without being decomposed. These compounds have been prepared by Sabanejeff,* who has analyzed them and found them to have the composition represented by the formula $C_2H_2I_2$. No attempt was made by him to determine their constitution.

In accordance with the Van't Hoff hypothesis, the solid acetylene di-iodide, which is much more stable than the liquid di-iodide would have the constitution represented by the formula—



$$\begin{array}{c} \mathrm{I{-}C{-}H} \\ \| \\ \mathrm{H{-}C{-}I} \end{array}$$

and would, therefore, belong to the same general class of acetylene derivatives to which fumaric acid belongs. Now, experiment shows that this solid acetylene di-iodide can be transformed into fumaric acid.

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* *Ann. Chem.* (Liebig), **178,** 118.

Nine grams of the acetylene di-iodide crystals (m. p. 73°) were dissolved in alcohol, and five grams (two molecules) of potassium cyanide added, and the solution was boiled for thirty-six hours in a flask with an inverted condenser. Caustic potash was thereupon added, and the boiling continued for two hours longer. On cooling the contents of the flask a considerable quantity of needle-shaped crystals separated from the liquid. They were removed from the solution, and on examination proved to be the potassium salt of fumaric acid, which crystallizes in the form of needles, insoluble in cold alcohol. More of the salt was obtained from the mother-liquor. The aqueous solution of the potassium salt was treated with silver nitrate and a white precipitate consisting of the silver salt was obtained. The silver salt was purified by dissolving it in nitric acid and reprecipitating it by carefully neutralizing the solution with ammonia. The silver salt of fumaric acid is characterized by its great insolubility in water, and by the fact that when it is heated it deflagrates like gunpowder. Both of these properties were exhibited by the silver salt of the acid made by synthesis.

A quantitative determination of the percentage of silver gave the following result:

·2039 gram of the salt, dried at 100° gave
·1786 gram of Ag Cl = 65·97 per cent. Ag.

	Calculated for $Ag_2 C_4 H_2 O_4$.	*Found.*
Ag, ...	65·43	65·97

The free acid itself was recognized by its insolubility in water; it was precipitated from moderately concentrated solutions of its salt by the addition of strong acids. It will be analyzed as soon as larger quantities of it have been obtained in pure condition.

In 1882, Sabanejeff* studied the action of potassium cyanide upon acetylene di-bromide and obtained an acid having the formula $C_4H_6O_5$. It is probable that fumaric or maleic acid was first formed in his experiments, which afterwards, by the prolonged action of boiling caustic alkali, was converted into the acid $C_4H_6O_5$. It has been shown by Linnemann and Loydl* that when fumaric acid is heated with caustic alkalis, it is gradually changed into an inactive maleic acid, thus:

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* *Ann. Chem.* (Liebig), **216**, 275.

$$\underset{\text{Fumaric acid.}}{C_4H_4O_4} + H_2O = \underset{\text{Inactive maleic acid.}}{C_4H_6O_5}$$

A more detailed study of the reactions, which gives rise to the formation of the two acetylene di-iodides, as well as the attempt to prepare maleic acid from acetylene, is reserved for future work.

BRYN MAWR, PA., February, 1890.

PROCEEDINGS.

[*Stated Meeting, held at the* INSTITUTE, *Tuesday, April 15, 1890.*]

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, April 15, 1890.

Mr. W. L. Rowland, Vice-President, in the Chair.

Members present: Dr. H. W. Jayne, Dr. Wm. H. Wahl, Prof. E. F. Smith, Messrs. W. W. Macfarlane, H. A. Galt, Reuben Haines, L. E. Williams, Lee K. Frankel, H. Pemberton, Jr., W. H. Bower.

The committee appointed at the preceding meeting for the purpose of selecting journals to be subscribed for by the Section made a valuable report, which was accepted by vote of the Section.

The members of this committee were Dr. Jayne, Dr. Hooker, Mr. J. H. Eastwick and Dr. Wahl.

The journals recommended were as follows: *Bulletin de la Société Chimique de Paris*, *Gazetta Chimica Italiana*, *Zeitschrift für Physiologische Chemie*, *Annalen der Chemie*, *Chemisches Centralblatt*, *Zeitschrift für Hygiene*, *Zeitschrift für Krystallographie und Mineralogie*, *Tschermak's Mineralogische Mittheilungen*.

The cost of these journals was estimated, approximately, at $50.

Dr. Jayne exhibited a fragment of what had been originally a lead wall in a tank in which chloride of calcium was employed for drying purposes; the lead had been converted gradually into chloride of lead crystals. Mr. Rowland mentioned a similar case in which the transformation of lead into chloride had been brought about by common salt on board a vessel.

Mr. Pemberton called attention to a recently patented improvement in manufacturing phosphorus; by this improvement a greater output per unit of heat was claimed.

Dr. Wahl exhibited a sample of aluminium electro-plating done by the Harvey-Filley Aluminium Plating Company, of Philadelphia. He called attention to the difficulties of aluminium plating in the past, and stated that they had been practically removed.

The monthly report of Dr. S. C. Hooker, on the Philadelphia Water Supply, was read by title, and referred for publication in the JOURNAL OF THE INSTITUTE.

Adjourned. WM. C. DAY, *Secretary*.

ON THE PRESENT CONDITION OF THE PHILADELPHIA WATER SUPPLY.

By SAMUEL C. HOOKER.

[*Presented at the Stated Meeting of the Chemical Section, April 25, 1890.*]

Since my third report was presented to this Section, a great deal of space has been devoted in the daily papers to the discussion of our water supply, and while one cannot but regret that much has been said which is both exaggerated and untrue, it is a matter for congratulation that the subject has once again been brought prominently before the public.

During a large portion of last summer, the water supplied to all parts of the city, without exception, was almost uninterruptedly muddy. Under these circumstances it is scarcely to be wondered that there should have been a disposition to make the worst of a condition of affairs certainly bad enough without the least exaggeration. It is too much to expect that the newspapers should possess in all or even in most cases the necessary knowledge to discriminate between facts which have and others which have no weight, between arguments and opinions, which are or are not entitled to consideration, and the result has been that an immense amount of misleading information, a vast number of positively incorrect and worse than valueless statements have been distributed broadcast to the public. Facts have been dwelt upon which have no weight, self-constituted authorities have been quoted whose statements have been remarkable for their inaccuracy, positively ridiculous for their scientific absurdity.

While, however, there has been unquestionable exaggeration in the arguments used against the water, there has also been a deplorable exhibition of bias and misinformation, and a positive disinclination to admit facts on the part of certain gentlemen, who appear to regard the present condition of our water supply as all that can be desired.

For three months, after the publication of my third report, I continued the laborious investigation, the early results of which have been already communicated to you. The publication of the numerous analyses has, however, been purposely delayed, because it was thought probable that they would be more fairly and impartially considered after the excitement, created by the newspaper agitation, had subsided. My analyses did not justify me in speaking as badly of the water as several of the newspapers were able to do, and any less vehement protest against its condition would have failed at that time to have attracted the attention which I hope will now be given to this paper.

In the following table will be found, as the condensed result of my investigation, average figures for the water collected at different parts of the city during six months of last year:

Samples Collected March to September, 1889.	Chlorine.	Free Ammonia.	Albuminoid Ammonia.	Nitrogen of Nitrates.
West Philadelphia, Forty-fourth and Chestnut Streets (24 samples), ...	·233	·0015	·0080	·099
Sixteenth and Locust Streets (23 samples), . . .	·254	·0014	·0081	·098
Twentieth Street and Columbia Avenue (23 samples), ...	·266	·0024	·0097	·100
Front and Bainbridge Streets (23 samples), . . .	·265	·0013	·0076	·099
Average of 93 city samples, ...	·254	·0016	·0083	·099

For purposes of comparison several samples of water were taken from the Schuylkill, at Phœnixville, in order that some idea might be formed of the extent of the pollution occurring within about 25 miles of the city. The samples from Phœnixville were furnished to me through the courtesy of the Water Department. For the other samples I am indebted to the kindness of several gentlemen residing in the various neighborhoods in which they were collected, who most cheerfully undertook the troublesome task of drawing the water for analysis at stated times.

Deferring for a moment the consideration of the Phœnixville samples and judging the water by such standards as are universally adopted, when the history of the water examined is entirely unknown, we are compelled to acknowledge that the above analyses do not in any way condemn the water, but, on the contrary, we must admit that the chlorine, free and albuminoid ammonias and the nitrates are present in quantities less than they are known to exist in many absolutely unpolluted waters.

By comparing the water at Phœnixville, however, with that supplied for city use, we are able to detect in the city water a slight increase in the quantity of the substances estimated, indicating that the sewage pollution, which we know exists, has occurred to an extent sufficient to appreciably influence the composition of the water.

The following table gives the average results of analyses of five samples of water obtained from each of the points named at nearly corresponding dates:

	Chlorine.	Free Ammonia.	Albuminoid Ammonia.	Nitrogen of Nitrates.
Phœnixville (average of 5 samples), ...	·196	·0039	·0079	.084
West Philadelphia, Forty-fourth and Chestnut Streets (average of 5 samples), ...	·227	·0022	·0101	·085
Sixteenth and Locust Streets (average of 5 samples), ...	·264	·0017	·0099	·088
Twentieth Street and Columbia Avenue (average of 5 samples), ...	·242	·0027	·0126	·086
Front and Bainbridge Streets (average of 5 samples), ...	·260	·0012	·0078	·083

Passing on to the discussion of each of the impurities determined, we may at once dismiss the nitrates from consideration, as the quantities present in the various samples of water examined differed only slightly from each other. It will be observed that the chlorine in the water drawn at all points of the city is greater than that found in the samples from Phœnixville.

Similarly the albuminoid ammonia in three out of the four localities in the city is distinctly greater than in corresponding samples from Phœnixville. With regard to the free ammonia a decrease in quantity is observed in the city water, but in spite of this, in view of the figures for albuminoid ammonia, we are compelled to regard the quantity of the organic substances discharged into the river after leaving Phœnixville, as somewhat greater than the combined action of the natural processes of purification and the subsiding reservoirs has been able to dispose of. During the six months covered by my investigation these impurities were almost entirely mechanically suspended, and by a suitable system of filtration could have been readily removed, leaving the water remarkably free from organic matter.

That most of the organic substances reaching the city should be pumped from the river in an insoluble form is not after all extraordinary. A considerable proportion of the organic matter of sewage exists of course in solution, but as many varieties of waste from as many factories, etc., are discharged into the river, it is probable that these substances, by acting and reacting on each other, give rise to the formation of precipitates, which in some cases may consist essentially of organic matters formerly in solution, in others which may mechanically enclose them. However this may be, the fact remains that the organic matter of the Schuylkill water, during the six months of last year that I investigated the subject, was almost and entirely in suspension and the condition of the water, deprived of its suspended matters, was entirely satisfactory, and often of a very high degree of purity.

Mud whether wholesome or unwholesome has obviously no place either in drinking water or in water to be used for household or industrial purposes, and to show, therefore, that the mud of the Schuylkill water is accompanied by precipitated organic matters derived from sewage, seems to me to add little to the many emphatic arguments, which can be already urged with unquestionable force against its presence being tolerated. But, on the other hand, by showing that practically the entire amount of the substances, which can be considered objectionable, are present in suspension and can be readily removed, leaving a water of a high degree of purity, how strong an argument we have for carrying out such purification.

In order that Schuylkill water may be filtered satisfactorily on a large scale, it is necessary to use a so-called "coagulant," and whether this be alum or iron, it is probable that the result will be much the same. Economical and mechanical considerations will have to be carefully weighed in choosing between them. The beneficial action of both these substances depends upon the formation of precipitates, which in the act of separation entrap and enclose the microbes and suspended particles, so that they can be arrested during subsequent filtration through sand. If the filtration be attempted without the addition of the coagulant, the very minute particles to which the turbidity of the water is due, pass through the interstices of the filter bed unchecked, but by first entrapping them in the precipitates derived from the coagulent used, they are virtually increased in size and can be arrested by the sand bed.

There is so much prejudice against alum, that it is desirable to discuss its use in the purification of water somewhat in detail. Alum is a double sulphate of aluminium and potassium and contains a large proportion of water of crystallization. Its percentage composition is as follows:

Sulphate of aluminium, ...	36·07
Sulphate of potash, ...	18·35
Water of crystallization, ...	45·58
	100·00

The sulphate of aluminium is the active portion of the alum and may be substituted for it if desired.

As soon as the alum is added to the water the carbonates present in solution react with the sulphate of aluminium, becoming themselves converted into sulphates with the formation of unstable carbonate of aluminium. The latter gives off carbonic acid gas and alumina separates. It is evident, therefore, that the separation of the alumina is not attended by the formation of free sulphuric acid, as has been alleged. The addition of alum to the water slightly increases the quantity of sulphates present and a small quantity of carbonate of lime is usually converted into sulphate of lime. The aluminium is entirely precipitated as alumina, and unless a considerable excess has been used, none whatever remains in solution.

I have dwelt upon the action of alum at so great a length (1) because I have been much impressed by the results which can be obtained by its use; (2) because it forms an essential feature of the American system of filtration; and (3) because I am convinced that the objections which have been urged against it are based upon an erroneous conception of its mode of action.

If it is the presence of microbes which is to be mainly feared in drinking water, there can be aside from boiling the water, no surer way of getting rid of them than by the use of a coagulant. The efficiency of iron for this purpose has been amply demonstrated at Antwerp and elsewhere; and in this country, Dr. Prudden, a well-known bacteriologist, of New York, has stated that he has found water purified by sand and alum filtration practically sterile. It has been frequently stated that microbes cannot be removed by filtration, that they will even pass a thousand abreast through the interstices of an ordinary sand-bed. In answer to this it may be said that while it is useless to look for good results by simple filtration at any speed which may be considered practical through clean sand alone, the matter is entirely changed by the use of a coagulant, and the smaller the particles, the more minute the microbes, the more surely are they entrapped in, surrounded and held by the precipitate formed.

The albuminoid ammonia in Schuylkill water, purified by sand and alum, has been often determined in my laboratory and has always fallen below ·0050 parts per 100,000.

There is scarcely a day when the water of Philadelphia does not reflect discreditably upon the city, its officials and its citizens. If we had but the one alternative, the use of the Schuylkill in its present condition or the expenditure of $20,000,000 to get water from elsewhere, we might possibly be excused for hesitation. But there are other ways of solving the difficulty. Water, considerably worse than that taken from the Schuylkill, has been successfully purified elsewhere, and why should not Philadelphia adopt a similar system of purification. It is evident that additional subsiding basins alone are impracticable for the work required. The enormous East Park reservoirs and the comparatively small amount of work they accomplish must have convinced all who have impartially considered the matter that some other method of purification must be adopted. The suspended matters of the Schuylkill water are mostly so minute and are deposited so slowly that very many times our present storage capacity would be necessary to render the condition of the water at all times uniformly clear and satisfactory. The large number and large size of the reservoirs required to do this and the immense outlay which their construction would involve would seem to be sufficient reason for looking to other methods of purification.

In conclusion, I desire to acknowledge my indebtedness to a gentleman who wishes to be nameless, not only for the interest he has taken in the progress of this investigation, but also for liberally sharing the expenses connected with it.

A complete list of my unpublished analyses of the Schuylkill water is appended.

ANALYSES OF THE PHILADELPHIA WATER SUPPLY.

Chlorine expressed in parts per 100,000.

1889.	Phœnixville.	West Philadelphia.	Sixteenth and Locust Streets.	Columbia Avenue.	Front and Bainbridge Streets.
May 24th,	—	·18	·28	·22	·30
31st,	—	·21	·25	·28	·24
June 7th,	—	·19	·20	·22	·20
14th,	—	·22	·24	·24	·24
21st,	—	·27	·26	·26	·31
26th,	·22	—	—	—	—
28th,	—	·27	·30	·33	·31
July 5th,	·16	·21	·26	·19	·23
12th,	—	·21	·23	·25	·22
19th,	—	·19	·20	·18	·20
26th,	—	·24	·24	·26	·26
August 1st,	·16	—	—	—	—
2d,	—	·21	·24	·15	·25
9th,	—	·21	·23	·26	·23
16th,	—	·20	·24	·19	·22
23d,	·18	·22	·24	·23	·21
30th,	—	·25	·23	·34	·28
September 6th,	—	·20	·28	·31	·30
7th,	·26	—	—	—	—
Mean of the above 16 analyses, May 24th—September 6th,	·196	·217	·245	·244	·250

ANALYSES OF THE PHILADELPHIA WATER SUPPLY.

Free Ammonia expressed in parts per 100,000.

1889.	Phœnixville.	West Philadelphia.	Sixteenth and Locust Streets.	Columbia Avenue.	Front and Bainbridge Streets.
May 24th,	—	·0010	·0005	·0020	·0010
31st,	—	·0005	·0010	·0035	·0005
June 7th,	—	·0000	·0010	·0020	·0005
14th,	—	—	—	—	—
21st,	—	·0017	·0005	·0015	·0020
26th,	·0012	—	—	—	—
28th,	—	·0049	·0010	·0049	·0010
July 5th,	·0079	·0027	·0022	·0030	·0012
12th,	—	·0005	·0015	·0030	·0005
19th,	—	·0017	·0017	·0022	·0050
26th,	—	·0040	·0025	·0020	·0017
August 1st,	·0054	—	—	—	—
2d,	—	·0012	·0044	·0030	·0022
9th,	—	·0007	·0022	·0027	·0022
16th,	—	·0022	·0027	·0067	·0020
23d,	·0040	·0000	·0002	·0015	·0002
30th,	—	·0007	—	·0025	·0029
September 6th,	—	·0024	·0007	·0015	·0015
7th,	·0010	—	—	—	—
Mean of the above determinations,	·0039	·0016	·0015	·0028	·0016

ANALYSES OF THE PHILADELPHIA WATER SUPPLY.

Albuminoid Ammonia expressed in parts per 100,000.

1889.	Phœnixville.	West Philadelphia.	Sixteenth and Locust Streets.	Columbia Avenue.	Front and Bainbridge Streets.
May 24th,	—	·0090	·0060	·0115	·0055
31st,	—	·0100	·0100	·0100	·0120
June 7th,	—	·0070	·0060	·0050	·0060
14th,	—	—	—	—	—
21st,	—	·0130	·0055	·0110	·0120
26th,	·0060	—	—	—	—
28th,	—	·0109	·0089	·0160	·0069
July 5th,	·0080	·0160	·0169	·0120	·0160
12th,	—	·0060	·0100	·0080	·0069
19th,	—	·0086	·0095	·0112	·0105
26th,	—	·0084	·0085	·0052	·0065
August 1st,	·0112	—	—	—	—
2d,	—	·0122	·0092	·0154	·0082
9th,	—	·0079	·0074	·0090	·0097
16th,	—	·0150	·0084	·0204	·0102
23d,	·0072	·0050	·0069	·0054	·0044
30th,	—	·0044	·0089	·0062	·0042
September 6th,	—	·0067	·0077	·0045	·0037
7th,	·0074	—	—	—	—
Mean of the above determinations,	·0079	·0093	·0085	·0107	·0081

ANALYSES OF THE PHILADELPHIA WATER SUPPLY.

Nitrogen of Nitrates expressed in parts per 100,000.

1889.	Phœnixville.	West Philadelphia.	Sixteenth and Locust Streets.	Columbia Avenue.	Front and Bainbridge Streets.
July 12th,	—	·098	·08	·108	·106
19th,	—	·092	·108	·08	·096
26th,	—	·11	·08	·13	·11
August 1st,	·064	—	—	—	—
2d,	—	·08	·098	·05	·092
9th,	—	·104	·08	·10	·108
16th,	—	·084	·078	·076	·104
23d,	·096	·088	·072	·108	·082
30th,	—	·103	·089	·110	·10
September 6th,	—	·088	·094	·10	·076
7th,	·092	—	—	—	—
Mean of the above analyses,	·084	·094	·086	·095	·097

PROCEEDINGS.

[*Stated Meeting, held at the* INSTITUTE, *Tuesday, May 20, 1890.*]

HALL OF THE FRANKLIN INSTITUTE.
PHILADELPHIA, May 20, 1890.

Mr. T. C. Palmer, President, in the Chair.

Members present—Dr. L. B. Hall, Prof. E. F. Smith, Dr. Wm. H. Wahl, Dr. H. W. Jayne, Mr. L. J. Matos, Mr. L. E. Williams, Mr. W. L. Rowland, Prof. Henry Trimble, Mr. Reuben Haines, Mr. W. H. Bower, Prof. R. L. Chase, Dr. S. C. Hooker, Mr. Hugh A. Galt, Mr. A. T. Eastwick, Mr. Fred. E. Ives, Mr. A. A. Moore and four visitors.

Mr. A. A. Moore, Franklin Sugar Refinery, Philadelphia, was elected an associate member of the Section.

Dr. Wahl read an interesting and valuable paper on "The Electro-deposition of Platinum."

The author prefaced this paper by the statement that at the next meeting he would exhibit specimens of substances employed in his investigation, and also illustrate the practical working of the processes described. The paper was referred for publication in the JOURNAL of the INSTITUTE.

Dr. Hooker presented a paper on "Derivatives of Lapachic Acid," and exhibited some beautiful specimens of these derivatives. The communication was referred for publication in the *American Chemical Journal.*

Adjourned.

WM. C. DAY,
Secretary.

PROCEEDINGS.

[*Stated Meeting, held at the* INSTITUTE, *Tuesday, June 17, 1890.*]

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, June 17, 1890.

Dr. H. F. Keller, Vice-President, in the Chair.

Members present—Dr. L. B. Hall, Dr. H. W. Jayne, Prof. R. L. Chase, Mr. G. L. Norris, Prof. E. F. Smith, Mr. Reuben Haines, Mr. A. A. Moore, Mr. H. Pemberton, Jr.

A letter from Dr. Wahl was received, announcing that indisposition prevented him from being present to read his paper illustrating the practical working of his process for the electro-deposition of platinum.

Prof. E. F. Smith read a valuable paper on the "Oxidation of Sulphur in Sulphides by Means of the Electric Current." The paper called forth some interesting comments from Drs. Hall and Keller and Mr. H. Pemberton, Jr. It was referred for publication in the JOURNAL OF THE INSTITUTE and in the *Berichte der deutschen chemischen Gesellschaft.*

Adjourned.

WM. C. DAY,
Secretary.

ON THE ELECTRO-DEPOSITION OF PLATINUM.

By Wm. H. Wahl.

[*Read at the Stated Meeting of the Chemical Section, May 20, 1890.*]

The permanence and unalterability of the metal platinum—properties which make it of such inestimable value to the chemist—have likewise suggested its application as a protective covering upon the surfaces of other metals; and, even in the early days of the art of electro-deposition, efforts to obtain a satisfactory coating of this metal were made. The failure with which these early experiments were attended, served rather to stimulate than to deter subsequent investigators, and the problem has received the attention of a number of the most noted experts in the art. The results that have been accomplished cannot be said to have been entirely satisfactory—a statement which, I believe, will be fully sustained by the fact that electro-plating with platinum, on the commercial scale, is practised only to a very limited extent. When the wide field of application for platinum-plating is considered—and I need only name philosophical, engineering, surgical, dental and electrical apparatus and instruments, fire-arms, watch-cases, and jewellery, to say nothing of the host of miscellaneous articles of utility and ornament to which the metal could be advantageously applied—the conclusion is warranted, that the processes thus far proposed for the purpose do not fully meet the requirements of practical service.

Thus far, of all the methods that have been proposed for electro-plating with platinum, three only appear to have sufficient merit to deserve special notice; these are:

(1) Roseleur-Lanaux' method, based on the electrolysis of a solution of the double phosphate of sodium and platinum.

(2) The process of the Bright Platinum Plating Company (of London), a modification of that of Roseleur, involving

the introduction into the bath of certain substances, such as sodium chloride and borax, to ensure a bright deposit of the metal; and

(3) Boettger's method, founded on the electrolysis of a solution of the double chloride of ammonium and platinum in sodium citrate.

Each of these baths will yield satisfactory results for a time; but, as I shall endeavor to show, the peculiar difficulties met with in the practice of platinum-plating render it impossible to maintain the chemical integrity of these electrolytes, and, in conseqence thereof, they soon become inefficient or inoperative by reason of contamination with the secondary products formed therein.

I will endeavor in what follows to give the true explanation of the difficulties above referred to, and to indicate what, from a careful study of the subject, fortified by the results of numerous experiments, I conceive to be the only feasible method of overcoming them.

The first difficulty encountered is that of obtaining a bright, reguline and adherent deposit of the metal, in which form only it will answer the demands of practice. There is no difficulty in effecting the separation of the metal from solutions of almost any of its compounds. Zinc, iron and tin reduce it promptly by simple immersion, and this very facility of reduction is one of the reasons why, even by the method of electrolysis, the desired object is frequently accomplished only in an imperfect manner; for the electroplater is obliged to meet and overcome its obstinate disposition to separate from many of its compounds in the condition of platinum black, lacking coherence and adherence, and therefore entirely unsuited for his purpose.

Another and no less serious difficulty arises from the insolubility of plates or sheets of this metal as anodes, when solutions containing platinum salts are submitted to electrolysis. In electro-plating with copper, silver, gold and nickel but little difficulty is encountered in practice on this account, since anodes of these metals are freely soluble in many solutions capable of depositing them when they are submitted to electrolysis, and the rate at which these anodes are respectively dissolved, approximates so nearly to that at which the metals are deposited upon the objects at the cathode, that the metallic strength of the electrolyte is maintained substantially constant, and electro-plating solutions of these metals may be operated for a long time without requiring additions of metallic salts. The electro-deposition of the metals whose anodes are thus tractable is carried on industrially with success.

It results from this want of solubility of the anode that the metallic strength of the electrolyte employed is continuously being weakened, while the deposition of the metal is going on, and the conductivity of the bath is being continually modified thereby. The character of the deposited metal also is injuriously influenced by these constant alterations of condition in the bath; and, as the rate of deposition becomes slower and slower by reason of the gradual impoverishment of the metallic strength of the solution, it becomes necessary to restore it by fresh additions of metallic salt. The practice in all the processes of electro-plating with platinum employed up to the present time, save that of Boettger, is to use for this purpose the tetra-chloride of platinum. With this single exception, all the solutions for the electro-deposition of platinum thus far made known, so far as I am aware, are made by treating the chloride with compounds of the alkalies, soda, potassa, or ammonia. Of these, the phosphates and oxalates of soda, or potassa, are in greatest favor, and a number of formulæ for preparing platinum-plating baths with their aid have been described. The resulting substance is commonly a double salt, such, for example, as the double phosphate of sodium and platinum; the double oxalate of potassium and platinum, etc., contaminated, however, in each case by the chloride of the alkali employed, which is formed from the decomposition of the platinic chloride. As often as it is found necessary to strengthen the bath, fresh additions are made of platinic chloride, which, by chemical interaction with the constituents of the bath, aided by the process of electrolysis, yields more alkaline chloride; and it follows that the bath, by reason of becoming surcharged with this foreign substance, and with other secondary products of electrolytic decomposition, ceases to yield bright, reguline platinum upon the articles to be plated therewith and must be discarded. It then becomes necessary to regain the platinum contained in the discarded bath, by one or another of several processes of reduction known to chemists. The platinum thus regained may be converted into chloride and utilized in the preparation of a fresh bath, with which the same series of operations may be repeated. Boettger purposes to maintain his bath by fresh additions of his original solutions, but it must be apparent that the continued electrolysis of such a solution as he employs must be attended with the constant accumulation therein of alkaline chlorides from the same causes as those specified above. This rapid deterioration of the baths, therefore, involves their frequent renewal at the expense of time and labor, so that, in spite of the fact that there is a wide field for its application, it is principally for this reason that the art of electro-plating with platinum on the commercial scale has thus far been practised only to a very limited extent.

It occurred to me that it might be practicable to overcome the principal difficulty here set forth. Knowing the influence of extent of surface in promoting the solubility of substances, it appeared to me at least probable that if the platinum were exhibited at the anode in the form of platinum-black, or sponge, exposing thus an enormously greater number of points of attack to the electro-negative element or acid radical there set free, the result might be the solution of the platinum, and the problem of maintaining the metallic strength of the electrolyte would thus be solved. The correctness of this conjecture was verified by experiment. For this purpose a plate of porous battery carbon, previously treated with boiling hydrochloric and nitric acids, was saturated repeatedly with a solution of platinic chloride and dried. It was then introduced into a graphite crucible, finely divided carbon was packed about it, and the crucible and contents heated for about half an hour to bright redness. The carbon plate then contained within its pores platinum in a state of eminently fine division. Treatment with water, and with hydrochloric acid at boiling temperature, failed to leach out any platinum salt, showing that the previous treatment had sufficed to reduce all the platinum salt to the metallic state. The carbon plate was then suspended as the anode in moderately diluted hydrochloric acid, a platinum plate serving as the cathode. The acid bath was gently heated and a current of moderate strength was allowed to flow through it. There was a liberal evolution of hydrogen from the cathode, but little perceptible evolution from the anode. The acid solution gradually became colored from the formation of platinic chloride, and after some time the bright surface of the cathode began to blacken and ultimately became covered with a thick coating of platinum black. It was thus demonstrated that an anode of platinum in the state of fine division is readily soluble in an electrolyte which yields chlorine at the anode when the same is electrolyzed. This observation, so far as I am aware, is new. It proved, however, to have no practical value, since the solution of the anode demanded the presence of a large proportion of free acid in the plating-bath and the use of current of such strength as to produce invariably the deposition on the surfaces to be plated, of black and non-adherent metal. Furthermore, it was found as was to have been anticipated, that the physical condition of the anode exerted no influence whatever in the electrolysis of baths formed of the oxysalts of platinum, from which the best results in electro-plating are obtained—since, in electrolyzing such compounds, the acid radical separated upon the surface of the platinum black failed to exert any perceptible solvent action.

It was therefore necessary to devise some other plan for overcoming the difficulties herein described, and, after making a number of fruitless experiments, I was so fortunate as to find a plan which appears to offer a solution of the troublesome problem of electro-plating with the group of metals, whose anodes are insoluble, in a more satisfactory manner than any other that has hitherto been suggested.

The plan here referred to consists in employing platinum hydroxide for the purpose of maintaining the metallic strength of the plating-bath. For this purpose, the hydroxide, which is readily soluble in alkalies and in many of the acids, may be introduced into the plating-bath from time to time and dissolved therein by stirring, or it may be permitted to remain in the bath in excess, the undissolved portion remaining at the bottom of the containing vessel, or it may be suspended in a canvas-bag adjacent to or surrounding the anode of carbon, according as the nature of the electrolyte may indicate one or the other method to be the preferable one. As the solutions which yield the best results in plating are those of the oxygen salts, I have found it advantageous also to prepare these directly from the hydroxide. This method, I have found, is capable of yielding a number of electrolytic baths of platinum that will maintain their metallic strength approximately unimpaired during electrolysis, and without the objectionable features of introducing into them substances that will cause them to deteriorate by the accumulation therein of injurious secondary products of decomposition, as is the case where such baths are maintained by additions of platinic chloride or alkaline chloroplatinates, as has hitherto been the invariable practice. Referring now specifically to the properties that render the platinic hydrate useful for the purposes above indicated, the following points appear to be deserving of mention.

It is readily soluble in aqueous solutions of the alkaline hydrates, and in a number of acids, mineral and vegetable In the treatment of the platinic hydrate with aqueous solutions of the alkaline hydrates, the former plays the part of a weak acid forming compounds known as platinates, which are very soluble, and from which the platinum is not precipitated on the addition of an excess of alkali. A weak aqueous solution of sodic or potassic hydrate (but especially the last named) will dissolve a large quantity of platinic hydrate, at the ordinary temperature, though solution takes place more freely, when heat is applied. These solutions, have the advantageous features of being freely conductive of electricity, and of yielding bright, reguline, and adherent electro-deposits of platinum on metallic surfaces previously prepared to accept the same. Furthermore, with a current of moderate strength, the platinic hydrate only is affected, as is shown by the pronounced evolution of oxygen at the anode and by the total absence of gas at the cathode. Also, it is manifest from the free solubility of platinic hydrate in alkaline hydrate, even in the cold, that if free platinic hydrate be present in a bath of alkaline platinate, the alkali set free in the process of electrolysis will combine with this platinic hydrate to form fresh platinate. For this purpose, it will be necessary either to have present in the bath at all times a small excess of platinic hydrate which may remain upon the bottom of the containing vessel, without interference with the plating, and which may be replenished from time to time; or, to introduce at the end of the day's work, a quantity of the platinic hydrate sufficient to restore the metallic strength of the bath to normal, assisting the solution of the metallic hydrate by stirring, and if necessary by the application of gentle heat. As I have found that the platinate solutions act best when they contain a considerable excess of free alkaline hydrate, being more conductive of the current and yielding the platinum more freely and in the best condition, the addition of the proper quantity of platinic hydrate at the close of the day's work in the case of a bath of considerable volume, or the addition of small quantities at intervals, in the case of a small bath, will be found to answer the desired purpose of maintaining the metallic strength of the bath approximately normal for an indefinite period. In a bath where considerable free alkali is present, the platinic hydrate added as just indicated, dissolves very freely even in the cold. The important fact is to be noticed, that the alkaline platinate solutions may be maintained and operated for a long time in the manner described, since no deleterious secondary products are formed by electrolysis to vitiate and render them inoperative, as will speedily be the case where the platinic chloride is used for this purpose. The mineral acids (hydrochloric, nitric, sulphuric, and phosphoric acids), dissolved the hydroxide freely, as likewise do certain of the vegetable acids, notably oxalic acid, and form with corresponding salts of the alkalies, double salts, many of which are soluble in water. Of the salts thus capable of being formed, however, so far as I have been able to determine by experiment, only a limited number appear to be adapted to yield a deposit of bright, reguline and adherent platinum. The halogen compounds may obviously be prepared more conveniently by the direct solution of the metal in *aqua-regia* than by the method I have described, but as I have found the oxygen compounds of platinum to yield much more satisfactory results, I therefore exclude them from consideration.

Of the salts that may be formed from platinic hydrate by solution in acids (and in part by suitable combination with the corresponding alkaline compounds to form double salts), three only may be named as sufficiently useful to yield practically valuable results in plating. These are the phosphates, oxalates and acetates, of which also it is practicable to form double salts with the alkalies, soda, potassa and ammonia, which yield bright, reguline and adherent plating.

Oxalic acid, so far as I have been able to determine, is, of all the oxygen acids, the best solvent of platinic hydrate, dissolving it even in the cold, but with great energy when aided by heat, and forming platinous oxalate, with evolution of carbonic anhydride. From this brownish-black or deep blue solution (according to concentration), brilliant reddish-brown scales of the salt separate abundantly and readily from the hot saturated solution. A saturated aqueous solution of the simple oxalate prepared from the hydrate as above described, will yield bright, reguline, adherent platinum when electrolyzed with a comparatively weak current, with evolution of carbonic anhydride at the anode. With a stronger current hydrogen also appears at the cathode. This bath may be maintained indefinitely at normal metallic strength by observing the precaution to add oxalic acid and platinic hydrate in small quantities from time to time; or by keeping constantly at the bottom of the bath some platinic hydrate, and adding oxalic acid in crystals or powder from time to time as may be required to keep the bath saturated; or, what is much to be preferred, making a supply of platinous oxalate from platinic hydrate in the manner previously described and keeping an excess of this present in the bath at all times. This bath has the same advantages as are possessed by the above-described alkaline platinate baths, of being capable of indefinite maintenance at normal metallic strength and of introducing no substances that will cause its deterioration by the formation of secondary decomposition products.

Phosphoric acid also is a solvent of platinic hydrate. A dilute aqueous solution of this acid will dissolve a small quantity of the metallic hydrate in the cold, and a much larger quantity when aided by heat. With increasing concentration, the solvent power of this acid for platinic hydrate is correspondingly increased. The resulting solution of phosphate of platinum according to the degree of concentration, will be wine-yellow to cherry-red in color, and with a comparatively weak current, will yield bright, reguline and adherent platinum on metallic surfaces properly prepared to accept the same. The electrolysis of this compound also, does not involve the formation of deleterious secondary products, the result of the operation being the separation of the metal at the cathode and of the acid radical at the anode—and of the elements of water which are evolved as gases respectively from anode and cathode. In the operation of the bath, therefore, it will become more and more acid as the metal is withdrawn by the accumulation therein of the phosphoric acid set free at the anode. The maintenance of the metallic strength of the bath, therefore, may be effected as in the foregoing cases by having present therein at all times a small quantity of platinic hydrate or by the addition at the end of each day's work of the quantity of the metallic hydrate which will be required to restore the amount of metal withdrawn. This bath must be worked very acid, and the solution of the platinic hydrate to maintain the strength of the bath must be facilitated by heating, as the solvent power of phosphoric acid for platinic hydrate is much inferior to that of oxalic acid. The double phosphates of platinum with certain of the alkalies may be formed, which will be capable of yielding a deposit of bright, reguline and adherent metal, and of being maintained approximately at normal metallic strength in the same manner as I have set forth above. I have obtained the best results with the ammonio-platinic phosphate, prepared by adding to the solution of platinic hydrate in phosphoric acid sufficient aqua ammoniæ to cause the same to give an alkaline reaction, which point will be indicated by the formation of a grayish precipitate that will not disappear on stirring; then restoring the acidity of the solution by adding free phosphoric acid in excess, upon which the precipitate readily dissolves. The resulting solution is yellowish or brownish, and yields superb plating; though, on account of the greater difficulty of maintaining its metallic strength by the solution of the hydroxide, it is not so well adapted as the oxalate for the work of electro-deposition on the large scale. The sodio-platinic phosphate, formed in a manner precisely analogous to the ammonia compound just described, will also yield bright, reguline and adherent plating; but I have observed that the soda salt is less freely soluble than the corresponding ammonia compound, and consequently more difficult than the latter to maintain of normal metallic strength.

Platinic hydrate is only very sparingly soluble in strong acetic acid, and it is impracticable to facilitate the solution by boiling, since by persisting in this for a very short time, the hydrate is decomposed and black platinic oxide is formed, which is quite insoluble in this menstruum. I have found, however, that an alkaline acetate bath may be prepared by the addition to the alkaline platinates above described, of as much acetic acid as may be introduced without causing the formation of a permanent precipitate. But although the appearance and quality of the plating obtained with this bath leave nothing to be desired, the bath does not meet the requirements in respect of indefinite maintenance in normal metallic strength and uniform composition. This difficulty, however, as I have observed, becomes less and less pronounced as the bath is made more strongly alkaline, when it approximates more and more closely to the alkaline platinates; for it is obvious that in the presence of a large amount of free alkali, this would unite with the acetic acid to form a simple acetate. The resulting solution would no longer contain sodio- (potassio-) platinic acetate, but sodic (potassic) acetate, sodic (potassic) platinate, and free alkali. Nevertheless, the presence of acetic acid in such alkaline bath appears favorably to influence the quality of the plating yielded, giving the deposited metal a whiteness approaching that of silver; and since furthermore, acetic acid yields only the elements of water and volatile compounds, when electrolyzed and therefore does not contaminate the electrolytic bath by forming deleterious secondary products, I find its judicious addition to the above-described alkaline platinate baths to present some advantages.

The foregoing comprise the compounds that I have found to yield the most satisfactory results in platinum plating, and I will not tax your patience at this time by an enumeration of the results, either partially successful, or wholly unsuccessful, that I have obtained with a number of differently constituted compounds of this metal.

I append directions for the preparation of the several electrolytic baths above described, and indicate what I have found to be the most favorable conditions for working them.

In conclusion, I desire to make known the fact, which was brought to my knowledge only within the past week, that my friend, Prof. Wm. L. Dudley, of Vanderbilt University, Nashville, Tenn., has independently worked out the problem of electro-plating with iridium in a manner precisely analogous to that which I have herein described with platinum. Prof. Dudley has made no publication of his research, but in a letter, informs me that he employed, as long ago as 1886, the following procedure, which I quote, "a bath of the metal may be composed of either the chloride ($IrCl_4$), the double chloride of iridium and sodium, or a double sulphate of iridium-ammonium. The latter was preferred. The bath was kept saturated with metal by suspending canvas bags in the solution (either near to or around the anodes) containing the hydroxide of iridium."

DIRECTIONS FOR PREPARING THE ELECTRO-PLATING BATHS.—For the alkaline platinate bath, the following directions may suffice:

Platinic hydrate,	2 oz.
Caustic potassa (or soda),	8 oz.
Distilled water,	1 gallon.

Dissolve one-half of the caustic potassa in a quart of distilled water; add to this the platinic hydrate in small quantity at a time, facilitating solution by stirring with a glass rod. When solution is effected, stir in the other half of alkali dissolved in a quart of water; then dilute with a enough distilled water to form one gallon of solution. To hasten solution, the caustic alkali may be gently heated, but this is not necessary, as the platinic hydrate dissolves very freely. This solution should be worked with a current of about two volts and will yield metal of an almost silvery whiteness upon polished surfaces of copper and brass, and quite freely. There should be slight, if any, perceptible evolution of hydrogen at the cathode, but a liberal evolution of oxygen at the anode. I have observed that the addition of a small proportion of acetic acid to this bath improves its operation where a heavy deposit is desired. The anode may be of platinum or carbon, and owing to the readiness with which the metal is deposited an excess of anode surface is to be avoided. Articles of steel, nickel, tin, zinc, or German-silver, will be coated with black and more or less non-adherent platinum; but by giving objects of these metals a preliminary thin electro-deposit of copper in the hot cyanide bath, they may be electro-platinized in the alkaline platinate bath equally well as copper. The bath may be worked hot or cold, but it is recommended to work it at a temperature not exceeding 100° F. It may be diluted to one-half the strength indicated in the formula and still yield excellent results. The surface of the objects should be highly polished by buffing, or otherwise, prior to their introduction in the bath, if the resulting deposit is designed to be brilliant.

The deposition of platinum takes place promptly. In five minutes; a sufficiently heavy coating will be obtained for most purposes. The deposited metal is so soft, however, that it requires to be buffed very lightly. A heavier deposit will appear gray in color, but will accept the characteristic lustre of platinum beneath the burnisher.

The oxalate solution is prepared by dissolving one ounce of platinic hydrate in four ounces of oxalic acid and diluting the solution to the volume of one gallon with distilled water. The solution should be kept acidified by the occasional addition of some oxalic acid. The simplest plan of using this bath, and which requires no attention to proportions, is simply to work with a saturated solution of the oxalate, keeping an undissolved excess always present at the bottom of the vessel. An addition of a small quantity of oxalic acid now and again will be found advantageous. The double salts of oxalic acid with platinum and the alkalies may be formed by saturating the bin-oxalate of the desired alkali, with platinic hydrate and maintaining the bath in normal metallic strength by the presence of an undissolved residuum of platinous oxalate.

The double oxalates are not so soluble in water as the simple salt. The oxalate baths, both of single and double salts, may be worked cold or hot (though not to exceed 150° F.), with a current of comparatively low pressure. The metal will deposit bright, reguline and adherent on copper and brass. Other metallic objects must receive a preliminary coppering as above. The deposited metal is dense, with a steely appearance, and can be obtained of any desired thickness.

The deposit obtained in the oxalate baths is sensibly harder than that from the alkaline platinate bath, and will bear buffing tolerably well.

The phosphate bath may be prepared by the following formula:

Phosphoric acid, syrupy (sp. gr. 1·7), ...	8 oz.
Platinic hydrate, ...	1–1½ oz.
Distilled water, ...	1 gallon.

The acid should be moderately diluted with distilled water, and the solution of the hydrate effected at the boiling temperature. Water should be added cautiously from time to time to supply that lost by evaporation. When solution has taken place, the same should be diluted with sufficient water to make the volume one gallon. The solution may be worked cold or warm to 100° F., and with a current much stronger than that required for the platinates and oxalates. The ammonio- (and sodio)- platinic phosphates may be formed from the simple phosphate by carefully neutralizing the solution of the phosphate with ammonia (or soda); then adding an excess of phosphoric acid, or enough to dissolve the precipitate formed and an additional quantity to ensure a moderate amount of free phosphoric acid in the bath. The phosphate baths will be maintained of normal strength by additions of platinic hydrate, the solutions of which will have to be assisted by heating the bath, preferably at the close of each day's work. The metal yielded by the electrolysis of these phosphate solutions is brilliant and adherent. It has the same steely appearance as that exhibited by the oxalate solutions, but to a less pronounced degree. The physical properties of the deposited metal are in other respects like those described in connection with that obtained from the oxalate baths.

THE OXIDATION OF SULPHIDES BY MEANS OF THE ELECTRIC CURRENT.

BY EDGAR F. SMITH.

[*Read at the Stated Meeting of the Chemical Section, June 17, 1890.*]

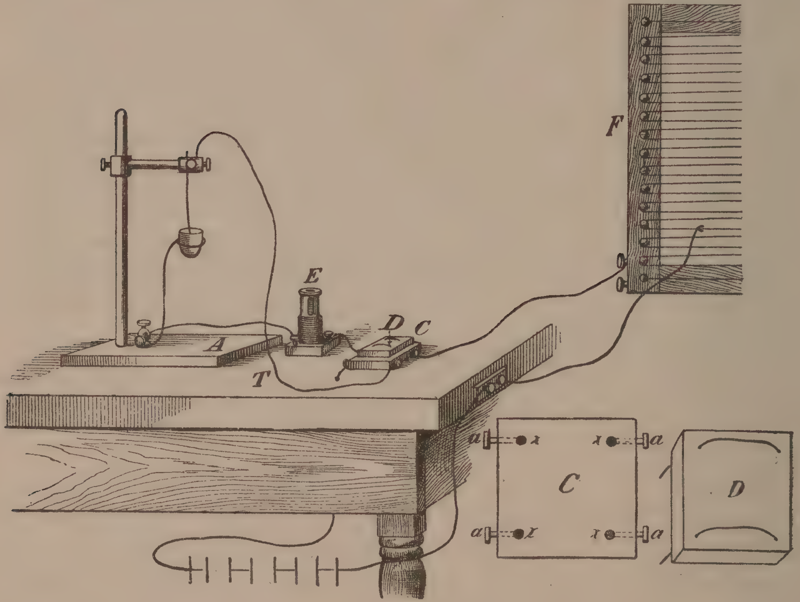
In the Proceedings of the Chemical Section of the FRANKLIN INSTITUTE, **1**, 52, and the *Berichte* **22**, 1019, a preliminary report was published, describing a rapid method for the conversion of sulphur into sulphuric acid through the agency of the electric current. It was there demonstrated that the sulphur in the mineral chalcopyrite, for example, was completely oxidized to sulphuric acid in ten minutes, and that the oxides Fe_2O_3, CuO, etc., were eliminated from the analysis, so that the barium sulphate finally weighed was perfectly white in appearance, and not contaminated with the impurities usually accompanying it when precipitated from solutions containing much iron, etc.

To give a better idea of the mode of carrying out an oxidation of this description, the apparatus used for this purpose will be first outlined.

T represents a table upon which stands *A*, an ordinary filter-stand, in the base of which is fixed a binding screw holding in position a heavy copper wire bent as seen in the sketch, and intended to carry the nickel crucible in which the oxidation occurs. The arm of the filter-stand has attached to it a binding screw holding a heavy platinum wire, as well as the copper wire generally in connection with the anode of the battery. *E* is a Kohlrausch ampèremeter, registering ampères and half ampères; this is in connection with *C*, a block of wood screwed or nailed to the table. There are four depressions (*x*) in *C* containing a few drops of mercury, in contact with the binding screws (*a*). *D* is the movable top of *C*; the wires crossing it project on the under side and rest in the mercury cups (*x*). When *D* is so arranged that the wires on its upper face run in the direction of the dart, the ↑ crucible becomes the anode of the battery, whereas if they have a horizontal position, ⟶ the crucible is the cathode.

F is a resistance frame, consisting of about 500 feet of common iron wire arranged upon a light wooden parallelogram. It should always be in the circuit.

The movable cap *D* is necessary and important. It enables the operator to change the poles quickly—to reverse the current at a moment's notice. In the oxidations to be described later on, this was frequently necessary, chiefly because when the crucible served as cathode in many of the decompositions there often occurred a considerable deposition of metal upon its sides, and in the act of separating this metal enclosed undecomposed material and withdrew it from the field of oxidation. In such cases, by making the crucible the anode, as above indicated, the mineral matter will be liberated, and upon coming in contact with a large oxidizing surface, all the sulphur contained in it will be converted into sulphuric acid. The crucible should always be covered during the oxidation.



OXIDATION OF THE SULPHUR IN SULPHIDES.

In the oxidations given later, nickel crucibles 1¼ inches high and 1⅜ inches wide were used; but a more advantageous form, one which should always be employed when more than 0·15 gram of material is used, would measure 2 inches in length and 1½ inches in width. In such a vessel, place 25–30 grams of pure potassium hydroxide (not sodium hydroxide), and warm the same until the excess of moisture is expelled. Bring the weighed sulphide into the crucible, connect the latter with the copper wire shown in the sketch, and lower the platinum wire so that it extends a short distance below the surface of the molten mass. The current is then made to pass by bringing a metallic cup, connected with one pole of the battery, in contact with one of the wires of the resistance frame *F*. The sulphur will be completely oxidized in from ten to twenty minutes. Interrupt the current, allow the crucible and contents to cool, then place the same in water. In a few minutes, all but the insoluble oxides will have dissolved. Filter, acidulate the warm filtrate with hydrochloric acid, and precipitate the sulphuric acid in the usual manner. If, upon adding acid to the alkaline solution the latter becomes turbid, from separated sulphur, it is an indication that the oxidation was incomplete. Observe closely whether sulphur dioxide is liberated even when the liquid remains clear. Never omit the examination of the residue remaining on the filter, after the alkaline solution has been filtered. The caustic alkali must always be tested for sulphur before using it in this work. It is well to estimate the impurities in the alkali and deduct them, in each determination, from the barium sulphate found.

To ascertain to what extent this method could be applied in oxidizing sulphur, the following minerals, representing all the various classes of natural sulphides, were subjected to experiment:

SPHALERITE (ZnS).

No difficulty was experienced in oxidizing the sulphur of this mineral. A current of one ampère (= 10·45 cc. electrolytic gas per minute) was amply sufficient for the purpose. When the mineral was added to the melted caustic potash and the current applied, the mass assumed a muddy appearance, which it retained for ten minutes when it became white and froth-like. It was discovered, by experiment, that this appearance indicated the complete oxidation of the sulphur.

(I) 0 1195 gram mineral, 20 grams alkali, 1 ampère (time, 20 minutes), gave 32·97 per cent. S.
(II) 0·1025 " " " " " " 32·96 "
(III) 0·1180 " " " " 10 " 32·80 "

By oxidizing the sulphur in a fourth portion with nitric acid and potassium chlorate, 32·90 per cent. sulphur was obtained.

A specimen of Joplin (Mo.) blende gave 32·60 per cent. and 32·80 per cent. S. by the nitric acid method, while by the electrolytic method 32·90 per cent. S. was found.

An impure sphalerite, locality unknown, in which there was considerable gangue and other admixtures, gave 29·8 per cent. S. when oxidized with nitric acid, and when acted upon in alkaline solution by a current giving one ampère of electrolytic gas per minute, the sulphur found was:

(I) 29·23 per cent. S.
(II) 29·45 " "
(III) 29·68 " "
(IV) 29·67 " "
(V) 29·90 " "
(VI) 29·58 " "

CINNABAR (HgS).

Very pure material was employed in this oxidation. Several trials were required, in order to learn the proper conditions for successful working. The tendency of this mineral, when finely divided, was to collect in lumps, which appeared to rise and fall in the alkaline solution; in order to bring every particle of material within the field of oxidation the current was reversed every few minutes. By doing this the sulphur was completely oxidized in twenty minutes or even in less time. If the precaution just mentioned with reference to the reversal of the current be not heeded more time will be required for complete oxidation and even then it will be doubtful whether the sulphur is fully converted into sulphuric acid. Twenty-five grams of caustic alkali were used in each experiment with this mineral.

0·1089 gram cinnabar gave 13·82 per cent. S., while the required percentage is 13·79.

A current of two ampères per minute was used.

GALENITE (PbS).

There is no difficulty in oxidizing this mineral. The same quantity of alkali and the same current strength were employed here as in the mineral immediately preceding:

(I) 0·1093 gram galenite gave	14·30 per	cent. S.
(II) 0·1092 " "	14·60 "	"

Another portion in which the sulphur was oxidized by heating the mineral in a current of chlorine gave 14·30 per cent. S.

ARGENTITE (Ag_2S).

No difficulty was encountered in oxidizing this mineral. The decomposition was made with conditions analogous to those already described. Silver did not pass into the alkaline solution, so that when the sulphuric acid was precipitated, barium chloride was employed as usual. The specimen analyzed being exceedingly pure, it was not thought necessary to determine the sulphur by any other method. None of it remained unoxidized:

0·1032 gram argentite gave 13·04 per cent. S; required 12·90 per cent. S.

CHALCOCITE (Cu_2S).

Thus far this mineral has resisted all efforts to convert its sulphur into sulphuric acid. Repeated attempts have been made, but not more than half of the sulphur contained in the mineral was oxidized, notwithstanding the current was very much increased in each trial. Since some time may elapse before another opportunity offers itself to continue experimentation with this mineral, it need only be stated that a modification of the usual method will be tried upon it. The copper and sulphur are evidently in very intimate union.

MOLYBDENITE (MoS_2).

The sulphur in this mineral is given up readily to the oxidizing influence of the current. One annoying feature is that the fine mineral particles are so very light that they are apt to be carried up and adhere to the cover crystal. In this oxidation the poles should be repeatedly reversed. The result given below is from a sample that contained much quartz, etc. The residue, however, gave not a trace of sulphur when tested for it.

0·1045 gram mineral gave 0·2785 $BaSO_4$ = 36·60 per cent. S.

STIBNITE (Sb_2S_3).

While a current of two ampères was employed in this oxidation, the sulphur can be completely changed to sulphuric acid with one ampère. Three trials proved this conclusively.

0·1095 gram mineral gave 0·2230 $BaSO_4$ = 27·91 per cent. S.; required sulphur, 28·5 per cent.

ORPIMENT (As_2S_3).

Pure material could not be obtained, so that the experiments were made with inferior mineral, and the greatest care was given the oxidation, so that sulphur was not afterwards discovered in the insoluble residue.

0·1150 gram sub. gave 0·2922 gr. $BaSO_4$ = 34·90 per cent. S.
0·1044 " " 0·2721 " = 35·79 " "

The arsenic was also oxidized to arsenic acid. Several tests proved the conversion to be quantitative. Results obtained in this direction will be published later.

JAMESONITE ($Sb_2S_5Pb_2$).

The sulphides of lead and antimony offer no difficulty in the oxidation of their sulphur. This sulpho-salt is decomposed with equal facility. A current of two ampères per minute was employed. The crucible was the anode for ten minutes, and the cathode for an equal period.

(I) 0·1078 gram mineral gave 0·1426 gr. $BaSO_4$ = 18·16 per cent. S.
(II) 0·1093 " " 0·1447 " = 18·18 " "
Required S = 18·30 per cent.

ENARGITE (AsS_4Cu_3).

The oxidation was made in the same manner as in jamesonite:

0·1102 gram mineral gave 0·2449 gr. $BaSO_4$ = 30·52 per cent. S.

A second sample, oxidized with nitric acid, gave 31·00 per cent. S.

STEPHANITE (Ag_5SbS_4).

This mineral was oxidized without difficulty. The conditions under which it was worked were similar to those of the preceding minerals:

(I) 0·1044 gram substance gave 16·69 per cent. S.
(II) 0·1109 " " 16·55 " " Theory req. 16·20 p. c. S.

KOBELLITE ($(Bi\ Sb)_2\ S_5\ Pb_2$).

The sulphur in this mineral was oxidized with ease:

(I) 0·1136 gram sub. gave 0·1562 gr. $BaSO_4$ = 18·38 per cent. S.
(II) 0·1157 " " 0·1594 " = 18·41 " "

The sample here oxidized was of the same material as that analyzed by Dr. Keller (*Proc. Chem. Sec. Franklin Inst.*, **1**, 127). On comparing the mean of his four sulphur determinations with the results obtained by the electrolytic method, it will be seen that the latter does not lack in completeness:

Current Oxidation.	*Nitric Acid Oxidation.*
Sulphur percentage.	18·37, 18·33, 18·46, 18·39
18·38—18·41.	Mean, 18·39 per cent. S.

TETRAHEDRITE $(Sb,As)_2S_7(Cu_2,Hg_2,Fe,Zn)_4$.

Quite a number of sulphur determinations and complete analyses of tetrahedrite of the above composition were made in this laboratory during the college year just closed. In all of these the chlorine method was employed for decomposition purposes. The percentage of sulphur found was 24·48 per cent. Samples of the same were then exposed to the action of a current of two ampères for twenty minutes, and the sulphuric acid determined in the usual manner with these results:

(I) 0·1073 gr. mineral gave 23·81 per cent. S.
(II) 0·1096 " " 24·38 " "
(III) 0.1086 " " 24·23 " "
(IV) 0·1095 " " 24·37 " "

Tetrahedrite seemed to require the full time (twenty minutes) for oxidation, for in several instances, where the current was interrupted after acting fifteen minutes, the alkaline solution became quite turbid upon acidulation.

STANNITE (SnS_4Cu_2Fe).

The conditions here were the same as those already mentioned for the other sulpho-salts:

(I) 0·1087 gram mineral gave 28·61 per cent. S.
(II) 0·1091 " " 28·02 " "

PYRRHOTITE ($Fe_{11}S_{12}$), MARCASITE (FeS_2) AND PYRITE (FeS_2).

The sulphur in the first of these three minerals is very readily changed to sulphuric acid. None of its iron passes into solution, so that the barium sulphate, after ignition, was perfectly white in color. The residue, not soluble in water, showed no unoxidized sulphur:

(I) 0.1087 gram mineral gave 0·3049 gr. $BaSO_4$ = 38·51 per cent. S.
(II) 0·1067 " " 0·3014 " = 38·79 " "

By oxidation with nitric acid the sulphur found was 38·78 per cent. S.

An exceedingly pure specimen of marcasite was exposed to the action of the current. Its sulphur was rapidly and completely oxidized:

0·1043 gram substance gave 0·4056 gr. $BaSO_4$ = 53·40 per cent. S. Required S. = 53·33 per cent.

While these sulphides of iron parted with their sulphur with great ease, pyrite held half of its sulphur content quite tenaciously, notwithstanding it was exposed to the influence of much more powerful currents than the other two minerals.

(I) 0·1667 gram pyrite and 20 grams KOH were exposed for ten minutes to the action of a current giving one ampère per minute. The crucible served as anode for half the time. The sulphur that was oxidized equalled 24·53 per cent.

(II) 0·3080 gram pyrite, 30 grams KOH, and a current as in (I) gave 22 per cent. S.

A number of similar trials gave about the same results. As chalcopyrite was oxidized without difficulty (*Proc. Chem. Sec.*, *Franklin Institute*, **1**, 53), the thought suggested itself that possibly the addition of cupric oxide might prove beneficial. Accordingly, the following experiments were made:

(III) 0·1009 gram pyrite, ·0611 gram CuO, 25 grams KOH, and a current of one and one-half ampères gave 36·39 per cent. S.

(IV) 0·1021 gram pyrite, ·0710 gram CuO, 25 grams KOH, and a current of one and one-half ampères gave 35·02 per cent. S.

(V) 0·1007 gram pyrite, ·0550 gram CuO, 25 grams KOH, and a current of one and one-half ampères gave 30·93 per cent. S.

The time in each trial was twenty minutes. While the addition of the cupric oxide apparently favors the sulphur oxidation, the results are anything but concordant.

(VI) 0·1000 gram pyrite, ·0950 gram CuO, 25 grams KOH, with a current of two ampères, for twenty minutes, gave 51·24 per cent. S.

(VII) 0·1000 gram pyrite, 0·1000 gram CuO, and other particulars the same as in (VI), gave 38·00 per cent. S.

The residues all contained unoxidized sulphur.

(VIII) 0·1045 gram pyrite, ·0523 gram CuO, 25 grams KOH, and a current of two and one-half ampères per minute, gave 46·93 per cent. S.

(IX) 0·1000 gram pyrite, ·0500 gram CuO, otherwise as in (VIII), gave 46·97 per cent. S.

(X) 0·1123 gram pyrite, 0·1400 gram CuO, 25 grams KOH, and a current of two and one-half ampères, gave 41·67 per cent. S.

(XI) 0·1160 gram pyrite, 0·1100 gram CuO, 25 grams KOH, and a current of two and one-half ampères, gave 51·26 per cent. S.

These examples are but a few of the many trials carried out to obtain all the sulphur. The final satisfactory results were obtained in the following manner:

(XII) 0·1060 gram pyrite, an equal quantity of cupric oxide, 28 grams KOH, and a current of four ampères per minute, gave 53·6 per cent. S.

The residue remaining, after treating the fused alkaline mass with water, was dissolved in nitric acid, diluted to 75 cc. with water, and tested with a solution of barium chloride.

No barium sulphate was precipitated on warming the solution, or even after allowing the same to stand for some days.

(XIII) 0·1048 gram pyrite, an equal quantity of cupric oxide, 28 grams KOH, and the current as in the preceding experiment, gave 53·02 per cent. S.

The residue did not contain sulphur. The time given for the oxidation in each of these experiments was twenty minutes, and the current was reversed after it had acted ten minutes.

Several trials were made with the view of ascertaining whether with conditions precisely analogous to those in the last two experiments, the copper oxide omitted, it would be possible to completely oxidize all of the sulphur. They proved failures. A current of five ampères, with cupric oxide absent, was insufficient for the complete conversion of the sulphur into sulphuric acid.

The sulphur of pyrrhotite was readily oxidized. Indeed, this mineral conducted itself very much like the monosulphides, zincblende, galenite, etc. Marcasite, too, offered no difficulty. Since it and pyrite differ only in crystalline form, can it be that the latter property alone is the cause of the greater stability of the pyrite? Will this explain its tenacious hold upon the sulphur? If this be true, why should not this stability extend to the two sulphur atoms? More than forty trials with pyrite show that it is only about half the sulphur which the current changes to sulphuric acid. At least such was the case when cupric oxide was not added. The same current strength that does this amount of oxidation with pyrite will convert *all* the sulphur in marcasite into sulphuric acid.

The writer would here acknowledge his indebtedness to Profs. Koenig and Keller for the mineral material consumed in this investigation, and also to Mr. D. C. Wallace for most valuable assistance in carrying out the oxidations and general analytical work.

University of Pennsylvania,
Philadelphia, June 7, 1890.

THE ELECTROLYTIC METHOD AS APPLIED TO PALLADIUM.

BY EDGAR F. SMITH AND HARRY F. KELLER.

[*Read at the Stated Meeting of the Chemical Section, March 18, 1890.*]

Our knowledge bearing upon the behavior of this metal towards the current is limited and rather indefinite. In 1868, Wöhler published, in the *Annalen*, **143**, 375, an article, entitled "Ueber das Verhalten einiger Metalle im elektrischen Strom," from which the following facts are taken · Palladium, as the positive pole of a battery, consisting of two Bunsen cells, was immersed in water acidulated with sulphuric acid, when the metal immediately became coated with a deposit having a bright steel-like color. This deposit is doubtless palladium dioxide, as it liberates chlorine when treated with hydrochloric acid, and carbon dioxide when warmed with oxalic acid. At the same time, black, amorphous metal separated upon the negative pole. Its quantity was slight. In the second edition of *Classen's Quantitative Electrolysis*, p. 72 (American edition), it is stated that a feeble current will deposit palladium in a beautiful metallic state from an acid solution. One Bunsen cell is given as sufficient for this purpose. A more energetic current produces a spongy deposit. Ludwig Schucht has communicated* that from an aqueous solution of palladious nitrate, acidulated with a few drops of nitric acid, the current precipitated upon the negative pole a bronze-colored deposit, which, as it grew more dense, became darker, and finally black in color. At the positive pole there was a simultaneous deposition of oxide, showing a reddish color. In alkaline palladic solutions the precipitation of metal was much retarded; the deposition of oxide was also observed.

Our first experience in the electrolysis of palladium salts was acquired from the double cyanide in an excess of potassium cyanide. In such solution a current, generating one cc. oxyhydrogen gas per minute, failed to cause metallic deposition until after the expiration of thirty-six hours; in other words, not until the excess of potassium cyanide had been completely converted into alkaline carbonates. Then the deposit was black in color, but the precipitation was not at all complete. No deposition of oxide was noticed upon the positive pole. The conduct of the metal in cyanide solution led to the trial of certain separations, the results of which will be given in a later communication. The action of the current (feeble) was also tried upon a solution of palladious chloride, in the presence of a large excess of potassium sulphocyanide. In this case the deposition of metal was exceedingly rapid. Spongy spots were noticeable. The deposit was black in color. The experiment was made with this solution in the hope that possibly a separation of copper from palladium might be found; but, as these metals separate with equal rapidity from their sulphocyanides, the results are valueless for this purpose.

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* Berg- und Hüttenmännische Zeitung **38**, 121; also, Zeit. für anal. Chem. **22**, 240.

The next attempt was made with palladammonium chloride, $Pd(NH_3)_2Cl_2$, in just sufficient ammonium hydroxide to retain it in solution. The total dilution of the solution was 125 cc.; the acting current gave 0·9 cc. OH gas per minute. The poles were distant from each other about two inches. Just as soon as the circuit was completed, a yellowish-brown coating appeared upon the spiral of the positive pole; while upon the dish, in connection with the negative pole, a deposit of metal closely resembling the platinum itself in color made its appearance. After acting through the night the current was interrupted, the metal deposit carefully dried and weighed. The precipitation was incomplete. It was, however, discovered that the deposition at the positive pole, which gradually increased in mass and assumed a black color, had entirely disappeared. In all instances where the ammonium hydroxide was in decided excess, the precipitation of oxide on the positive pole was not observed. This behavior is similar to that of nickel when its ammoniacal solutions are electrolyzed. In subsequent experiments the course was somewhat modified. From solutions such as just described, the palladium thrown out upon the platinum dish was extremely slow in dissolving, even in fuming nitric acid, so that it was deemed expedient to first coat the platinum dishes employed in the electrolysis with a layer of silver, varying in weight from 0·1 to 0·3 gram. This was done in the experiments recorded below, and was found to be decidedly advantageous. The layer of silver seemed to hasten the deposition of the palladium.

EXPERIMENT I.

A quantity of palladammonium chloride (= 0·2228 gram Pd) was dissolved in ammonium hydroxide; to this solution were added 20 to 30 cc. of the same reagent (sp. gr. 0·935) and 75 cc. water. The current allowed to act upon this ammoniacal liquid gave 0·9 cc. oxyhydrogen gas per minute. The decomposition continued through the night. At no time was there any oxide deposition upon the anode. The palladium gradually assumed a bright metallic appearance. After drying, the deposit showed about the same appearance as is ordinarily observed with this metal in sheet form. The washing was limited to hot water, and when the deposit was perfectly dry, the dish containing it was covered with a watch glass and exposed to a temperature ranging from 110° to 115° C. This was done to expel any hydrogen that might possibly have been retained by the palladium.

Weight of silvered dish + Pd = 61·9575 grams.
" " " — Pd = 68·7350

0·2225 Pd.

EXPERIMENT II.

In every respect similar to Experiment I, gave

Weight of silvered dish + Pd = 71·9540 grams.
" " " — Pd = 71·7315

0·2225 Pd.

The filtrates from these deposits were warmed for eight hours with ammonium sulphide without showing any formation whatever of palladium sulphide.

In several experiments, with conditions unlike those just described, and where consequently an incomplete precipitation of metal occurred, the digestion with ammonium sulphide produced in every instance, in a very short time, a reddish-brown flocculent sulphide, carrying with it quite a considerable quantity of free sulphur.

In a second series of two experiments, in each of which there was the same amount of palladium as in the previous trials, the quantity of ammonium hydroxide in excess was made 30 cc., while the current (giving 0·8 cc. oxyhydrogen gas per minute) was allowed to act for sixteen hours. The results were quite concordant:

EXPERIMENT III.

Weight of silvered dish + Pd = 72·1055
“ “ “ − Pd = 71·8825

Weight Pd = 0·2230 gram.

EXPERIMENT IV.

Weight of silvered dish + Pd = 62·0512
“ “ “ − Pd = 61·8280

Weight Pd = 0·2232

It may be remarked that in filling the silvered platinum dishes a rather large surface of silver was allowed to remain above the electrolyzed liquid, so that by merely adding water it was possible to ascertain when the palladium was fully precipitated. When the deposition was not finished, the new silver surface soon showed streaks of metal.

A third series of two experiments, in which the added amount of palladium was double that recorded in the preceding examples, the same conditions were observed as before, with the exception that as the current was only giving 0·70 cc. oxyhydrogen gas per minute, the time of precipitation was extended to eighteen hours. The results were as follows:

EXPERIMENT V.

Weight of silvered dish + Pd = 72·3555
“ “ “ − Pd = 71·9100

Weight Pd = 0·4455

EXPERIMENT VI.

Weight of silvered dish + Pd = 62·2600
“ “ “ − Pd = 61·8138

Weight Pd = 0·4462

Curiously enough, upon warming the liquid poured off from the palladium in Experiment V, with ammonium sulphide there appeared a very slight sulphide precipitate after some hours. The liquid from Experiment VI showed no trace of unprecipitated metal.

The deposits in the experiments just recorded were bright, metallic and very dense. In none was there the slightest tendency to sponginess. To show the accuracy of the method, the results may be tabulated as follows:

Experiment.	*Found Pd.*	*Calculated Pd.*
I,	0·2225	0·2228
II,	0·2225	0·2228
III,	0·2230	0·2228
IV,	0·2232	0·2228
V,	0·4455	0·4456
VI,	0·4462	0·4456

If the percentage differences be calculated, it will be found that they are quite within the limit of error occurring in almost any ordinary gravimetric determination.

The behavior of ammoniacal palladium solutions, when exposed to the action of the electric current, will be further studied as time permits, and, if possible, the attempt will be made to re-determine the atomic weight of the metal by this method in a somewhat modified form.

UNIVERSITY OF PENNSYLVANIA,
PHILADELPHIA, February 12, 1890.

PROCEEDINGS.

[*Stated Meeting held at the* INSTITUTE, *Tuesday, September 16, 1890.*]

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, September 16, 1890.

Mr. T. C. Palmer, President, in the Chair.

Members present: Prof. E. F. Smith, Mr. Reuben Haines, Dr. D. K. Tuttle, Prof. N. Wiley Thomas, Mr. A. A. Moore, Mr. Lee K. Frankel, Dr. Wm. H. Wahl, Mr. Fred. E. Ives, Prof. R. L. Chase, Mr. A. T. Eastwick, Mr. G. L. Norris and four visitors.

Dr. Tuttle proposed the name of Mr. Cabell Whitehead, of the Mint Bureau, of Washington, as an associate member of the section; the name was referred to the Committee on Admissions.

Dr. Wahl presented the paper by Dr. Masser, of Los Angeles, Cal., on "The Curve of the Elements," which was to have been read by Dr. Persifor Frazer. It was read by title, and on motion it was decided to refer the article to a special committee for publication. The President named Dr. Wahl, Dr. Hall and Prof. Smith as members of this committee.

Mr. Reuben Haines then read a thoroughly-prepared paper on "The Use of Galvanized Iron in the Conveyance of Drinking Water." Some interesting results of the analysis of water conveyed in galvanized pipes were presented, and also a careful review of the most important literature on the subject. The paper was referred for publication in the JOURNAL.

An interesting discussion followed in regard to the immunity enjoyed by workmen engaged regularly in handling poisonous metals and their compounds. Dr. Wahl instanced, as a remarkable example of this, the continual inhalation by the workmen in the galvanizing works of zinc chloride vapors, produced by throwing ammonium chloride upon the surface of the molten zinc in the operation of galvanizing iron.

Dr. Tuttle called attention to the carelessness in regard to health shown by workmen in white lead works. Remarks were also made by the president and by Mr. Reuben Haines.

Adjourned. WM. C. DAY, *Secretary.*

PROCEEDINGS.

[*Stated Meeting, held at the Institute, Tuesday, October 21, 1890.*]

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, October 21, 1890.

Mr. H. Pemberton, Jr., in the Chair.

Members present: Messrs. Wahl, Smith, Hooker, Hall, Sadtler, Haines, Frankel, Tuttle, Williams, Galt, Jayne, and a number of visitors.

Dr. Wahl presented a paper, by Dr. Hans von Strombeck, on "The Constants of Ammonia," and proposed its reference to a committee for examination with a view to its publication.

The Chair appointed Messrs. Rowland, Wahl and Hall as the committee.

Prof. Sadtler presented and made some remarks in regard to a paper on "Utah Ozokerite." Specimens were exhibited to the Section. The material was said to be obtained in quantities. Prof. Sadtler spoke of some of the uses of ozokerite obtained from Hungary.

Prof. Smith read a paper giving some of the results of a preliminary study by Dr. Keller and himself on the action of sulphydric acid on certain amines.

The paper was referred for publication.

Adjourned. H. W. JAYNE, *Secretary pro tem.*

ON THE USE OF GALVANIZED IRON FOR ARTESIAN WELLS AND FOR THE CONVEYANCE OF DRINKING WATER.

By REUBEN HAINES.

[*Read before the Chemical Section, September 16, 1890.*]

The writer recently received for analysis for potability a sample of water from an artesian well, which proved to be of somewhat unusual character. The well had been sunk a few months ago on a homestead property, situated a short distance beyond the northern boundary of this city. It was seventy-eight feet in depth, and the outer casing as well as the inner tube were of galvanized iron.

The water had been previously analyzed by another chemist and was pronounced by him to be contaminated with sewage. As no source of contamination was known to exist near the well, it was thought a mistake had been made.

My analysis showed, however, that water contained an enormous amount of free ammonia, and also an extraordinarily large amount of zinc in actual solution.

I subsequently learned that the pipes were discovered to be very much corroded in the short time they had been in use.

The following are the results of my examination of the water:

Composition—

	Parts per 100,000.
Free ammonia,	0·4730
Albuminoid ammonia,	0·0080
Chlorine,	0·80
Total solid matter at 100° C.,	15·50

Nitric Acid, { Only faint traces by the acid phenyl sulphate test in 100 cc. in column seven inches in height in a colorless glass tube.

Sulphuric Acid (qualitative).—Small traces or none at all.

Injurious Metals, { Large amount of zinc in solution; identified by several appropriate tests.

Appearance.—Clear and colorless, there being no turbidity, no sediment deposited until exposed to the air for several days, when white flakes were observed at the bottom of the bottle.

Taste.—After taste, very slightly astringent.

I subsequently determined the amount of the zinc in the remaining portion of the same sample, and found it contained 3·9 grains of the oxide of zinc per gallon, equivalent to 3·12 grains of metallic zinc. As this portion of the water was small, only one-quarter liter, I was unable to make a complete analysis, but in the following statement have supplied by calculation the amounts of sodium and carbonic acid, assuming that all the chlorine was combined with sodium only, and that zinc calcium and ammonia existed wholly as carbonates; the small traces of sulphuric acid, nitric acid and magnesia, if present, being neglected altogether. This, I think, must be at least approximately correct, as the evaporated solids yielded considerable carbonic acid on treatment with HCl. The results are as follows:

	Grains per Gallon.
SiO_2, Al_2O_3, and Fe_2O_3,	0·85
$NaCl$,	0·77
$CaCO_3$,	1·30
$(NH_4)_2CO_3$,	1·25
$ZnCO_3$,	6·52
Total solids,	10·69

The total solids by actual weight in this portion were equivalent to 10·56 grains per gallon dried at 100° C.

In the above analysis it will be observed that the free ammonia is the only positive evidence of organic contamination in this water. The albuminoid ammonia, however, while scarcely excessive for a medium quality and usable surface-well water, seems rather too large for a deep well in the rock. The albuminoid ammonia should not exceed 0·0050 parts per 100,000, and is frequently not more than 0·0030, if the water is absolutely secure from contamination. The amount of chlorine is not more than is natural for many pure and soft well waters. The freedom from nitrates is rather remarkable, there being less than is found in some of the purest spring waters.

I ascertained that there was no cesspool drain, manure heap, or any other source of contamination within 200 feet of this well. At that distance there is a stable, but the stalls are drained by a cemented terra-cotta pipe, which is carried to a considerable distance further away from the well. As regards surface drainage, the well is favorably situated, being on higher ground than the stable. The nearest source of contamination on the adjoining premises is at least 500 or 600 feet distant.

In every respect, therefore, so far as known, the well appears to be properly protected as regards location. As, however, the well is deep and the amount of water abundant, it is reasonable to conclude that a water-bearing stratum draining a very large area, or perhaps a strong flowing underground stream has been tapped. Hence, the water may have become contaminated by sewage at a very great distance from the well. Such instances have been known to occur. In this way I am inclined to account for the free ammonia in this water, which has possibly been increased by reduction of nitrates previously present in the water, induced by contact with iron and zinc.

There can be no doubt that the water has been, somewhere in its course, contaminated with a large amount of nitrogenous organic matter, probably animal sewage.

A peculiar feature of this water is the large amount of zinc which it contains, and the fact that the whole of it is in solution. On heating or partial evaporation, the zinc separates as a film on the surface of the water.

That water has a solvent action upon metallic zinc has been known for a long time. As early as 1778 it was alluded to by M. de la Falie, a French physician and chemist. Thenard and Gay Lussac and, in 1813, Vauquelin and Deyeux reported upon it to the French Academy of Sciences. Chauffèle, in 1848, and Payen and Chevallier, in 1854, confirmed it experimentally as regards ordinary water and even distilled water. Similar results have been reported by others since that time. In most of these cases, only traces or very small amounts of zinc were dissolved. Prof. W. R. Nichols, of Boston, some fifteen years ago, stated that he always expected to find zinc in water which passed through galvanized iron pipe. He found that Lake Cochituate water, which had remained undisturbed in pipes at the Massachusetts Institute of Technology for thirty-six hours, the pipes having been in use for eight or nine years, contained a small amount of zinc in suspension, and 0·062 grain per gallon in solution.

In another case, when the analysis of the water gave suspicious evidence of contamination with sewage, he found a trace of zinc in suspension, and 0·843 grain per gallon in solution.

The mode of action of common potable water on zinc is understood to be, first, the formation on the surface of the metal of a coating of oxide of zinc, which is then acted upon by the carbonic acid generally present in the water, converting it into a mixture of oxide, carbonate and, according to Pettenkoffer, an oxyhydrocarbonate, or as now termed, hydrated basic carbonate, which gradually becomes more or less separated from the metallic surface and is carried in suspension or forms a film on the surface of the water, while a small part dissolves.

In the case before us, I think the oxide and carbonate of zinc have combined with the carbonate of ammonia to form the double carbonate of zinc and ammonia, which is insoluble in water, but very soluble in carbonate of ammonia, the excess of carbonate of ammonia in the water thus holding it in solution. This combination of salts is decomposed by boiling water or by heating on the water bath.

I found that both commercial zinc and chemically pure zinc, each in the coarsely "granulated" or feathered condition, were rapidly acted upon by a cold dilute solution of carbonate of ammonia, from which, after twenty-four hours' contact with zinc, a copious precipitate of zinc sulphide was thrown down by H_2S after acidifying with acetic acid.

It is not unusual to find considerable zinc in suspension either as hydrated oxide or carbonate in waters, for instance, that have been retained for some time in galvanized iron, "circulating boilers" in dwellings, especially in the case of new boilers.

I once had in my possession a piece of lead pipe which had connected a "circulating boiler" to the "water-back" of the kitchen range, and which at one point was almost completely stopped up with a reddish-white deposit; and this deposit proved to be composed principally of oxide and carbonate of zinc, derived, no doubt, from the galvanized iron boiler.

I have also observed in one instance a scum or film of zinc hydrocarbonate almost completely covering the surface of the water in a cedar tank after the water had entered this tank through several hundred feet of galvanized iron pipe leading from a spring-house. The spring water had been until near that time quite pure, but was contaminated during heavy rains by a shallow well a few feet distant, which contained decaying vegetable matter and the water of which yielded a large amount of free ammonia, but gave no evidence of sewage pollution.

There can be no doubt that, like the case of the artesian well before us, the excessive amount of ammonia in the spring water had a solvent action on the zinc coating of the galvanized pipes, but that on free exposure to the air in the tank the hydrocarbonate of zinc was separated, as it appeared in a crystalline film on the surface of the water.

The amount of zinc thus carried into the water, either in suspension or in solution, appears to depend not only on the impurities in the water, but also upon the quality of the galvanized iron; both as to whether the process of coating with zinc has been properly done and as to the purity and texture of the zinc itself. If, for instance, the iron has been allowed to become spotted with rust, even if the rust is apparently well cleaned off before dipping the iron surface into the zinc bath, a more rapid corrosion, it is said, is liable to occur when the zincked article is immersed in water.

As regards the injurious effects of potable water containing zinc, the zinc oxide or carbonate carried in suspension in any large amounts would not be likely to cause trouble to health, because most people would usually refuse to drink any water so turbid without filtering it. Hence, only the smaller amounts of suspended zinc and that which is in solution need be considered.

While it is true that in the case of the artesian well described in this paper no chemist would be likely to advise the use of this water on account of the strong suspicion of sewage contamination, yet it is suggestive of possibilities where the water is not submitted to a chemist for examination.

An interesting paper on the use of zincked or galvanized iron for the storage and conveyance of drinking water was contributed by Dr. W. E. Boardman, of Boston, to the Fifth Annual Report of the Massachusetts State Board of Health, 1874, the object of which was stated to be to determine, if possible, whether such use of this material was attended with danger of zinc poisoning, this having been asserted in the Boston *Journal of Chemistry*, in commenting upon cases of illness occurring at Spot Pond, Melrose, Mass., in 1871.

To this paper I refer as a concise statement of the opinions of numerous distinguished authors from 1795 to 1872.

"From this *résumé* of opinions and facts," says Dr. Boardman, "it may be confidently asserted that the oxide of zinc *as it occurs in drinking water* is absolutely harmless."

With regard to the carbonate of zinc, he says: "The almost universal testimony appears to point conclusively also to the innocuity of this compound."

The above conclusions are in regard to that which is in suspension only. As regards the effects of zinc in a soluble form, Dr. Boardman says: "Admitting, then, that water which has been stored in reservoirs or drawn through pipes of galvanized iron always contains zinc in solution in the form of one or more of its salts, the innocuity of those salts *in the quantities in which they occur* is attested by the experience and experiments of the various distinguished observers to whom we have already referred. While they admit the deleterious influences which may be occasioned by the soluble salts of zinc when taken internally in sufficient quantity or for a long time, they are unanimous in the recommendation of the use of zincked iron for the storing and conveyance of water." [*The italics in the above quotations are the writer's.*]

In most of the cases considered only a very small amount of zinc was found in solution; and Dr. Boardman expressly states that he does not include in his consideration the effects of waters obviously unfit for drinking on account of sewage pollution or other abnormal qualities.

Dr. Boardman, in the above-mentioned *résumé*, has followed the older writers on *Materia Medica*, but since the publication of his paper opinion seems to have become somewhat modified.

Dr. Bartholow, in his work on *Materia Medica and Therapeutics* (3d ed., 1880, p. 229, *et seq.*) says of the physiological action of the salts of zinc: "The preparations of zinc are active in proportion to their solubility and power of diffusion. The chloride sulphate and acetate are the most active, and in the order in which they are placed; the carbonate and oxide being insoluble have very feeble diffusive power and possess consequently very slight activity."

"Long-continued use of the sulphate, even in small medicinal doses, may excite ulceration of the mucous membrane. The oxide and carbonate, although insoluble and inactive, slowly produce systematic effects."

"All of the salts of zinc when long continued may produce a train of symptoms not unlike those caused by lead, viz: Emaciation, pallor, loss of strength, constipation and colic, muscular weakness and trembling, paralysis, etc."

"The oxide in large doses and used for a long period has produced wasting and fetid breath, gastro-intestinal catarrh, weakness and feeble mind."

"The zinc salts manifest much less tendency to accumulate, and are excreted much more rapidly than mercury, lead and copper."

The symptoms above described by Dr. Bartholow are, of course, to be understood as produced by very much larger quantities of zinc than ordinarily occur in water. Nevertheless, the older opinion of the almost absolute innocuity of the more insoluble forms appears to be seriously questioned, and our sense of security is correspondingly somewhat disturbed.

That zinc may also occur in a soluble form in drinking water in quantities which may be almost called medicinal is shown by the analysis of this artesian well water. It is now well known that, as regards lead, the long continued daily use of water containing a small fraction of a grain of the metal in a gallon has had distinctly marked effect upon the system, and the chemist is advised to condemn a water carrying more than one-tenth of a grain per gallon. This is largely in consequence of the cumulative power of this metal. Zinc not possessing that power in so great a degree is proportionately less injurious.

It is true that large communities have been accustomed to drinking water slightly contaminated with zinc without any effects being apparent that could be attributed to it. Thus we may instance a large experience in this city and vicinity.

And, again, I find in *The Analyst* (vol. iv, p. 51), an abstract of a paper by E. Hylius, in which he says that the presence of minute quantities of zinc does not seem so injurious to health as is generally believed. That author analyzed a sample of spring water from Tuttendorf, in Germany, and found it to contain 0·007 grams of zinc oxide per liter, equal to 0·49 grains per imperial gallon; and he was assured that the water had been drank by the population for about a century.

This sort of evidence is, however, not conclusive by itself, for many obscure symptoms which may really be caused by small amounts of metallic poisons are liable to be attributed to a variety of other causes. The same argument may be used with regard to a public water supply from a river decidedly polluted with sewage. In the absence of an epidemic, it is often very difficult either to prove or disprove the precise deleterious effects of a sewage polluted water supply on the population of a large city.

In the same manner it has been shown that in the case of a town in Scotland, supplied with water containing a very large amount of sulphate of lime, the inhabitants did not appear to suffer any injurious consequences from drinking such a water. Yet it is a well-established opinion among sanitarians that excessive amounts of sulphate of lime in drinking water are undoubtedly productive, as a *general fact*, of diseases of the digestive organs.

Still it must be conceded that the weight of practical opinion is decidedly on the side of the innocuity of the use of galvanized iron for water pipes. Thus, as a result of a discussion at a meeting of the German Society of Gas and Water Engineers, H. Bunte collected in 1887 information to show that the use of galvanized pipes should be in no way detrimental to health. Dr. V. Ehmann, late Director of the Water Supply of Würtemburg, stated that objection to such pipes cannot be taken on sanitary grounds, and he considered them peculiarly suitable for use in the interior of buildings.

English authors on sanitation have always been opposed to the use of zinc for roofs which are to be utilized for the collection of rain water for drinking and culinary purposes.

Neither should lead or lead-coated sheet iron, called terne plate, for roofing purposes be used under such circumstances. Sheet copper is equally objectionable. All these metals or metallic combinations, if unprotected by a suitable paint, will be corroded by the free acids frequently found in the atmosphere of rural localities as well as of cities; and, also, by the ammonia always more or less present in rain water, which exerts a solvent action upon copper. The corrosion of copper by the impurities of rain water is known from practical experience with copper-roofed buildings in Europe.

In conclusion, therefore, it may be said that while under usual conditions of water-supply with pure water galvanized iron pipe may be advantageously used for its conveyance without detriment to health; yet, too much confidence should not be placed upon it. All the conditions under which the zincked pipe is to be used should be carefully considered, including a chemical analysis of the water; and, in the presence in the water of considerable amounts of certain saline substances, such as ammonia salts, chloride of sodium and nitrates, as well as very small amounts of free mineral acids, etc., galvanized iron should not be used at all. Under such circumstances, only pipes coated with a non-metallic interior surface should be used.

UTAH OZOKERITE.*

By Alfred N. Seal, S.B.

[*Read at the Stated Meeting of the Chemical Section, October 21, 1890.*]

Ozokerites, in general, have been quite frequently studied, but Utah ozokerite has not been very fully investigated, and the results which have been published are of a conflicting nature. Prof. S. B. Newberry publishes † certain results as follows: "Its melting point is 61°·5.

Composition—

C,	86·15
H,	13·75
	99·90

It distils without decomposition, is not altered by strong acids or by hot alcohol, but is soluble in ether, turpentine or naphtha." He considers it a mixture of paraffines, possibly containing some admixed olefines. Wurtz, ‡ depending almost entirely upon calculations of analyses made by other chemists, pronounces the material to be an olefine. He states in proof of this that he has found the action of sulphuric acid upon it to be violent, with copious evolution of SO_2. He also states that the material does not crystallize from solvents, thus differing from the paraffines. As will be shown, the work which was here done upon this substance disproves several of the statements made above.

The material is of a dark brown color, of wax-like consistency, and has a foliated structure. Occurring with it were bundles of crystals of a white fibrous mineral, which showed by analysis that it was gypsum. The melting point is 53° to 55°; the specific gravity ·9285. The material is easily soluble in warm benzene, petroleum spirit, ether and carbon bisulphide. The dilute solution is highly fluorescent.

Alcohol precipitates a solid from the solution in benzene, and when the precipitation is carried on slowly, most of the coloring matter comes out with the solid first precipitated, leaving a more or less clear solution. This, of course, shows that the coloring matter is less soluble in alcohol than the light colored solid which finally comes down with excess of alcohol. This is contrary to the result of Beilstein* with Caucasian ozokerite, he stating that the coloring matter is the more soluble of the two substances.

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* Abstract of a thesis for degree at the University of Pennsylvania.

† *Eng. and Min. Jour.*, March 22, 1879.

‡ *Eng. and Min. Jour.*, July, 1889.

On boiling a portion of the ozokerite with absolute alcohol and then chilling the liquid, a pure white solid separated out in pearly scales, while the black residue sank beneath. The extraction was never complete, the residue, after having been subjected to this treatment in an extractor for two days, still showing traces of the white material, thus thwarting all attempts at obtaining a quantitative estimate of the amount of the white material in the ozokerite. However, by chilling the solution from the extractor, filtering, drying and weighing the white solid, it was found that at least sixty per cent. of the ozokerite consisted of this white hydrocarbon. This white material was further purified by dissolving in boiling absolute alcohol, allowing all traces of oily material to settle, and then pouring the clear solution through a warm filter. This filtrate, when chilled, gave the white solid in waxy plates.

By combustion, this hydrocarbon showed the following composition. Weight of substance taken, ·2013 grm; weight of CO_2 found, ·6297 grm., corresponding to ·1720 grm. C., weight of H_2O found, ·2603 grm., corresponding to ·0291 grm. H.

C.	85·44
H,	14·45
	99·89

A second analysis was as follows: Weight of substance taken, ·1797 grm.; weight of CO_2 found, ·5622 grm., corresponding to ·1536 grm. C.; weight of H_2O found, ·2352 grm., corresponding to ·0262 grm. H.

C,	85·47
H,	14·57
	100·04

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* *Ber.* **16,** 1574.

This white hydrocarbon, when melted, became of a yellowish color, of a waxy constituency, and had the specific gravity ·9708. It was easily soluble in all the solvents mentioned for the crude ozokerite, and in addition was soluble in hot absolute alcohol and in hot acetone.

To ascertain whether this substance was a saturated or an unsaturated hydrocarbon, a solution of it in CS_2 was treated on the water bath with a solution of bromine in the same solvent, the latter allowed to run in slowly. There was no decolorization of the bromine solution, no fumes were given off and apparently no action took place. This indicates that the material is a saturated hydrocarbon. Two grammes of the white material were then treated with about 15 cc. of concentrated H_2SO_4. No action took place in the cold. The flask was then heated for two hours at 75° and then for a few minutes at 100°. Only a very faint odor of SO_2 was perceptible. A large excess of water was then added and the whole warmed, well shaken and then chilled. The cake of wax which rose to the top was darker in color, but not blackened. The filtrate was neutralized with $PbCO_3$ and filtered. The solution was then evaporatedto dryness, when a very small amount of a yellowish salt, insoluble in water, remained. This marked resistance to the action of a strong acid indicates that the material is a paraffine.

The white hydrocarbon when highly heated broke up into an oily mass and a solid, together with carbon, and had an empyreumatic odor.

To determine, if possible, the molecular weight of the hydrocarbon, the Raoult method was employed. The apparatus recommended by Beckman was used, with a thermometer graduated to tenths. The solvent used was benzene which had been purified by crystallization, the freezing point of which was 5°·5. Tetra- and di-bromdiacetyl were used in standardizing the solvent. The results were as follows:

					MOLECULAR WEIGHT.	
	C.	*L.*	*P.*	*A.*	*From Formula with 49 as constant.*	*Theoretical.*
$C_4H_2O_2Br_4$, .	·4	13·9240	·4233	·1315	371	370
$C_4H_4O_2Br_2$, .	·47	17·0325	·3240	·2470	198	212

Hence, in working with the paraffine, the factor 49 was employed as given by Raoult for neutral organic substances with benzene as the solvent.

In trying to employ the method with the paraffine, great trouble was experienced, the solubility of the substance in benzene at 5° being so slight that it was necessary to have a solution so dilute, that the depression of the freezing point was only ·1°. On using a less dilute solution, the paraffine separated out in the form of a jelly, when the solution was cooled. The results were as follows:

C.	*L.*	*P.*	*A.*	*M.*	*Average for M.*
·1	14·8625	·0853	·1742	280	256
·1	26.2820	·1253	·2097	233	—

Four grammes of the crude ozokerite were treated with concentrated H_2SO_4 in the same way that the white hydrocarbon had been. A decided odor of SO_2 was noticeable, but no such fumes or violent action as noticed by Wurtz was observed. A white granular residue, weighing about ·2 grs., remained on evaporating the neutralized filtrate. This indicates that there was contained in the crude ozokerite a small proportion of olefines, which were attacked by the sulphuric acid. The small amount of a salt obtained from the white hydrocarbon was probably due to the fact that a complete separation had not been effected by the means employed.

A yellow, oily material, with a melting of about 40°, was obtained as a residue in the purification, since its solubility in hot alcohol was less that of the white hydrocarbon. This could not be obtained pure in sufficient quantities to warrant an investigation, but its properties would seem to indicate that it was an olefine.

The results given evidently do not agree with those given by Wurtz. The main mass of the ozokerite is not readily attacked by reagents, and does crystallize very readily from solvents. This is sufficient proof to show that it is a paraffine. The melting point and percentage composition of the hydrocarbon would designate it as one of the higher paraffines, and would place it about $C_{25}H_{52}$. The molecular weight, as given by the Raoult method, would give about $C_{18}H_{38}$. The true formula, if it is a simple body, probably lies between these two.

No attempt has been made to deduct the chemical nature of the material from the analyses, since, with so great a molecular weight, a difference of two hydrogen atoms, necessary to distinguish a paraffine from an olefine could not be determined.

The specimen of ozokerite upon which this investigation was made was furnished me by Dr. Sadtler, under whose direction the work was carried out, and to whom, as well as to Dr. Keller, my thanks are due.

UNIVERSITY OF PENNSYLVANIA, June, 1890.

PROCEEDINGS.

[*Stated Meeting, held at the Institute, Tuesday, November 18, 1890.*]

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, November 18, 1890.

Mr. T. C. Palmer, President, in the Chair.

Members present: Dr. L. B. Hall, Dr. H. W. Jayne, Mr. H. Pemberton, Jr., Mr. C. J. Semper, Dr. S. C. Hooker, Dr. Wm. H. Greene, Prof. E. F. Smith, Mr. Reuben Haines, Mr. W. W. Macfarlane, Mr. A. A. Moore, Dr. Wm. H. Wahl, Mr. Philip S. Clarkson, and a number of visitors.

The election of Mr. Cabell Whitehead, of the Mint Bureau at Washington, as an associate member of the Section, was announced.

Mr. Pemberton nominated Mr. Richard D. Baker, 216 South Third Street, Philadelphia, as a member of the Section. The nomination was referred to the Committee on Admissions.

A letter from Mr. Heyl, the Actuary of the Institute, was read, in which certain recommendations were made relative to the course to be pursued in paying bills for journals, etc., the contracting of which had already been formally sanctioned by the Section. The views expressed met with the approval of the Section and the Secretary was directed to so inform the Actuary.

On motion of Mr. Pemberton, it was voted that the Secretary of the Institute be authorized to renew the subscriptions to the journals aken by the Section.

Prof. Smith moved that the Section subscribe for the Bulletin of the French Chemical Society; the motion was carried.

At the suggestion of the treasurer it was voted that he be authorized to purchase 1,000 envelopes for the use of the Section.

On motion of Mr. Pemberton, it was voted that the Section suggest to the Library Committee of the Institute the propriety of completing the sets of all the journals taken by the Section.

The report of the Committee on the Publication of the Paper by Dr. Masser, of Los Angeles, Cal., on "The Curve of the Elements," and also another by Dr. Hans von Strombeck, of New York, on "The Constants of Ammonia," was accepted and the committee was discharged.

On motion of Dr. Wahl, it was voted that a committee be appointed to prepare a circular-letter addressed to chemists at large, setting forth the facilities possessed by the Section to receive, examine and publish promptly papers of meritorious character on chemical subjects.

In this circular-letter, he proposed also to call attention to the fact that a number of printed copies of an accepted paper would be returned to the author, within two weeks of the date of its acceptance by the Section; and furthermore to the fact that the publications of the Section are forwarded promptly, as advance sheets, to the leading chemical journals at home and abroad.

The following nominations of officers for the ensuing year were then made: For President, Dr. Wm. H. Wahl; for Vice-Presidents, Mr. H. Pemberton, Jr., and Dr. Wm. H. Greene; for Secretary and Treasurer, the present incumbents in each case; for Conservator, Dr. Wahl.

Dr. Greene then presented a paper by himself and Dr. Wahl, on "Alloys of Sodium and Lead." It was referred for publication in the Journal.

Dr. Greene also stated that he would submit a number of specimens of new alloys proposed by the authors at the next meeting.

Dr. Wahl then read an abstract prepared by Prof. C. F. Himes, of Carlisle, describing a new photographic process without the use of metallic salts, based on the light sensitive properties of primuline. It was referred for publication. In connection with this paper Mr. Macfarlane stated that the active substance of the process, known as "primuline," and the primuline dyes in general, had been abandoned in dyeing, because of the fact that they would stand exposure to direct sunlight for only a short time before fading out.

Dr. Jayne called attention to a chart illustrating clearly the details of the new process for manufacturing nitric acid, invented by Oscar Goodman, and recently described in various journals.

Mr. Palmer exhibited a piece of logwood which was unusual in presenting a bronzy green surface, such as is commonly found only in chipped wood that has been put through the process of curing. This fragment was part of a log six feet in length, taken from a wind-shaken tree through which rain-water had percolated. The rain-water, probably by the action of the ammonia contained in it, had produced a result analogous to that secured by the usual curing process.

Adjourned. WM. C. DAY, *Secretary.*

ALLOYS OF SODIUM AND LEAD.

By Wm. H. Greene and Wm. H. Wahl.

[*Read at the Meeting of the Chemical Section, November 18, 1890.*]

Recently, in the course of certain investigations, in which we had occasion to make use of alloys of lead and sodium, we found that the properties of such alloys did not correspond with what we had anticipated from previous publications on the subject, and we were led to an examination of the properties of lead-sodium alloys of definite composition. These alloys may easily be made by direct combination, and the products are then sensibly constant in composition, which is not the case when they are prepared by reducing lead oxide by carbon in presence of soda, or by heating litharge with sodium tartrate, as described by Vanquelin and Serullas.

The required quantity of sodium was added to lead melted in a covered crucible, and the alloy was roughly analyzed by determining lead only. Our alloys contained from three to thirty-one per cent. sodium. They are all brittle and crystalline; all decompose water, that containing the least sodium producing a hardly perceptible evolution of gas, while that containing thirty-one per cent. reacts with violence. The brittleness and oxidability increase with the percentage of sodium. The richest alloy is greenish in color and instantly blackens on exposure to air.

We made special examinations of the alloys corresponding in composition to Na_2Pb_2, Na_2Pb and Na_4Pb: the first of these contained ten per cent. sodium, the second 19·5 per cent, rather more than would be indicated by the formula, while the last contained 31·7 per cent. The densities were determined in aniline and found to be considerably higher than would be the densities of mixtures of the same composition. Thus the ten per cent. alloy has a density of 6·91, the 19·5 per cent. a density of 4·61, and the 31·7 per cent. alloy a density of 3·81. The densities of corresponding mixtures would be 5·6, 3·7 and 2·7, respectively.

The theoretical and calculated percentages of Na in alloys of above assumed composition compare as follows:

	Na_2Pb_2	Na_2Pb	Na_4Pb
p.c Na by theory,	10	18·18	30·8
" found,	10	19·5	31·7

THE ACTION OF HYDROGEN SULPHIDE GAS UPON METALLIC AMINES.

BY EDGAR F. SMITH AND HARRY F. KELLER.

[*Read at the Stated Meeting of the Section, held October 21, 1890.*]

When pure, dry hydrogen sulphide gas was conducted over palladammonium chloride, $Pd(NH_3Cl)_2$, no change occurred in the appearance of the compound. However, on applying a gentle heat (70°–80° C.) to the boat containing the metallic amine, the latter gradually assumed a black color. This change extended throughout the entire mass. Upon increasing the heat ammonium chloride was volatilized. The residue was found to consist of palladium and sulphur. Single mineral acids were without effect upon it. Aqua-regia attacked it very slowly.

(I) — 0·3790 gram of $Pd(NH_3Cl)_2$ gave 0·2498 gram of the black sulphide. Assuming that the latter is represented by the formula PdS, the required monosulphide for the quantity of palladammonium chloride used would be 0·2484 gram.

(II) 0·2795 gram $Pd(NH_3Cl)_2$ gave 0·1822 gram sulphide, while the calculated amount should be 0·1831 gram.

This behavior of the palladammonium chloride led us to expose the following metallic amines to the action of hydrogen sulphide gas:

PURPUREO-COBALTIC CHLORIDE (Co_2Cl_6, $10NH_3$).—0·5287 gram of this substance, finely divided, were weighed out in a porcelain boat. The latter was placed in a combustion tube of hard glass. This was in connection, on the one side with a drying apparatus, on the other with a Peligot tube containing water. The latter served to produce a back-pressure of the gas, and in this manner the boat and its contents were constantly surrounded by an atmosphere of hydrogen sulphide. The gas was at first allowed to act in the cold. It produced an immediate change. The cobalt amine assumed an intense black color. To all appearances the change was complete in a few minutes, and extended through the entire salt. On the application of a gentle heat (80°) ammonium chloride volatilized. Later the heat was raised, and a current of carbon dioxide substituted for the hydrogen sulphide. The boat was allowed to cool down in this gas. The final product was dense, and black in color. Its weight was 0·2258 gram. Assuming the change of the amine was to sesquisulphide the amount of the latter, corresponding to 0·5287 gram of the amine, would weigh 0·2253 gram. On examining the sulphide it was found to consist of sulphur and cobalt.

ROSEO-COBALTIC SULPHATE ($Co_2(SO_4)_3, 10NH_3 + 5H_2O$).—This salt, too, sustained an immediate change when acted upon in the cold by hydrogen sulphide. There was in addition a simultaneous evolution of moisture, and stellated, colorless crystals appeared on the walls of the combustion tube. These gradually dissolved in the water present, and imparted to it an intense yellow color. The crystals were $(NH_4)_2S_2$. On gently heating roseo-cobaltic sulphate in a stream of hydrogen sulphide, it invariably happened that when a temperature of 70° C. was attained, the black mass, in the boat, swelled up considerably, and was projected into the tube. Some deep-seated change occurred, which we are not prepared to explain at present.

LUTEO-COBALTIC CHLORIDE ($Co_2Cl_6, 12NH_3$).—This salt was affected by hydrogen sulphide in the cold, although heat was required to bring about a complete change. One quantitative determination gave the same result as was obtained with purpureo-cobaltic chloride, *i. e.*, the product was evidently cobalt sesquisulphide.

Of the cobalt amines examined, the roseo-derivative was most rapidly changed by the gas. We have good reasons for believing that we can make this reaction serviceable in the determination of cobalt in these bases.

PURPUREO-CHROMIC CHLORIDE ($Cr_2Cl_6, 10NH_3$).—We exposed this salt for a long period, in the cold, to the influence of hydrogen sulphide, without its sustaining any alteration. On raising the temperature so that it was slightly lower than the dissociation temperature of hydrogen sulphide, the purple-colored amine became quite black in color. It had a velvety appearance and resembled the chromium sesquisulphide obtained by other methods.

(I) 0·6390 gram substance gave 0·2640 gram sulphide. The theoretical amount should be 0·2629 gram.

When this sulphide is exposed to a high heat in a current of hydrogen gas, it parts very slowly with its sulphur.

It is our intention to apply this reaction to other metallic amines as soon as we can do so, though at present our work has been interrupted by unforeseen circumstances.

UNIVERSITY OF PENNSYLVANIA,
PHILADELPHIA, October 17, 1890.

A NEW PHOTOGRAPHIC PROCESS WITHOUT METALLIC SALTS.

This process was presented at the recent meeting of the British Association for the Advancement of Science, by Mr. A. G. Green, and his co-laborers, Messrs. Cross and Bevan, in a paper detailing highly successful experiments with primuline for producing designs on cotton, linen or silk cloths, on paper, and, by aid of gelatine, on glass, etc., by a "photographic method of dyeing and printing." The process requires no longer time of exposure than that with silver salts, whilst it has a more general range of sensitiveness in the spectrum, and at the same time affords the choice of a great variety of colors for the finished prints; and as primuline is a commercial article used on a large scale, it is comparatively inexpensive. The process will only be outlined in brief. Primuline, a coal-tar product, is an amido-sulphonic acid discovered by Mr. Green, in 1887, and named by reason of the primrose yellow color imparted by it to cotton in alkaline solution, without a mordant. It has been quite extensively used for producing a great variety of colors in cotton cloth by *diazotizing* the compound in the cloth dyed with primuline, by passing it through a weak solution of nitrous acid, or rather of a nitrite with an acid, and thus imparting to it the property of combining with various phenols or amines to produce in the fabric a variety of highly colored, very fast dyes—the so-called ingrain colors, the particular color in any case being determined by the phenol or amine employed in solution rendered acid or alkaline as may be necessary. It was found that the diazotized compound is extremely sensitive to light, which destroys this property of combining with the phenols and amines, so that a fabric dyed with primuline, then washed and treated with nitrite of soda and acetic acid, and again washed, and then exposed, either moist or dry under any design, as a drawing or a negative, will lose the property of becoming dyed by the phenols and amines in the parts acted upon by light, so that in a subsequent treatment with a suitable amine or phenol, as a developer, only the protected parts will become dyed, and a print will be produced having the positive or negative character of the original. Thus the lines of a drawing will be reproduced in color. By selection of the suitable developer not only one of a great variety of colors may be given, but by applying two developers, mixed with starch paste locally by means of a brush, two colors may be produced in the same fabric. The fixing of the print is accomplished by simply washing it with water. The following developers were given: For *red*, an alkaline solution of beta-naphthol; for *maroon*, of beta-naphthol-disulphonic acid; for *yellow*, of phenol; for orange, of resorcin; for *brown*, a solution of phenylene-diamine hydrochloride; for *purple*, a solution of alpha-naphthylamine hydrochloride. Paper for copying plans, etc., may be coated by means of a brush or roller. The process is in its tentative stage and full of promise in many directions. According to an article in the *British Journal of Photography*, based on further experiments, and giving working formulæ, the dressing should be removed from ordinary muslin for use by this process; the exposure required is less than with ordinary albumenized paper, but negatives of greater density are required; and, what is of highest interest, a simple aqueous solution of either of the common photographic developing agents, eikonogen and pyrogallol, will act as an energetic developer, the former giving the much desired ink-black tone and the latter a brown tone. C. F. H.

ON SOME CONSTANTS OF AMMONIA.*

BY DR. HANS VON STROMBECK.

[*Read at the Stated Meeting of the Chemical Section, October 21, 1890.*]

If we have to calculate the dimensions of a refrigerating machine it is absolutely necessary to know the exact value of the heat of evaporation (latent heat) of the liquid by means of which the cooling effect is produced. Though in these calculations all designers take the heat of evaporation of liquid ammonia to be about 540 English or 300 French thermal units, nevertheless many of them claim the heat of evaporation of ammonia to be in reality about 900 English or 500 French thermal units. The reason for this assertion is that on being determined the first time the heat of evaporation was found to be about 500 French thermal units. But, as afterwards it was proven that the ammonia used in this test contained a good deal of water, H. V. Regnault repeated the tests with ammonia, absolutely free of any moisture, and found the average figure of the heat of evaporation to be 294·2 French thermal units. To prove once more that this latter figure is correct, and also to decide some other questions relating to ammonia, at the suggestion of Mr. Louis Block, Chief Engineer of the De La Vergne Refrigerating Machine Company, I determined by a series of tests:

(1) The specific heat of liquid ammonia;

(2) The total heat, heat of evaporation and heat of liquid of ammonia;

(3) The heat of absorption of ammonia;

(4) The heat of combination of liquid ammonia and water.

To this is added:

(5) A table showing the difference in the figures for the total heat of evaporation and the heat of absorption.

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* From the laboratory of the De La Vergne Refrigerating Machine Co.

I.—DETERMINATION OF THE SPECIFIC HEAT OF LIQUID AMMONIA.

The determination was made in the usual way: The steel cylinder (μ_2) containing the liquid ammonia (M) was suspended in a jacketed drum and heated up to a certain temperature ($T + \delta_1$) by means of the vapor of boiling methylic alcohol which circulated in the jacket. After the liquid ammonia was heated up to a constant temperature, which took about six hours, the steel cylinder (μ_2) with its contents (M) was quickly put in the brass calorimeter (μ) which was filled with a certain quantity of distilled water (m) of a certain temperature (t). By the heat given to m and μ by M and μ_2, the temperature of the water rose from t degrees to $\tau + \delta$ degrees. From the figures thus obtained the specific heat of the liquid ammonia can be calculated.

In the following, all temperatures are in degrees Celsius, all weights in grammes, all measures in cubic centimetres, all thermal units are French ones. The liquid ammonia used in all the following tests was manufactured in the gas plant of the De La Vergne Refrigerating Machine Company.

Its composition was:

99·926 per cent. ammonia;
0·055 per cent. mineral oil (liquid base) which originates from a patented process used in the manufacture of the liquid ammonia;
0·019 per cent. moisture.

If, in the following:

M = the weight of the gaseous and liquid ammonia and its contaminations in the steel cylinders;
$M - \mu_3 - \mu_4 - \mu_6$ = the weight of the liquid ammonia;
m = the weight of the water in the calorimeter;
μ = the weight of the brass calorimeter and the metal part of the agitator;
σ = its specific heat;
$\mu\sigma$ = its value in water;
$\mu_1\sigma_1$ = the value in water of the thermometer in the calorimeter;

μ_2 = the weight of the steel cylinder;

σ_2 = its specific heat;

$\mu_2 \sigma_2$ = its value in water;

v = the contents of the steel cylinder in cubic centimetres;

$\varepsilon (T + \delta_1)$ = the specific gravity of liquid ammonia at $T + \delta^1$ degrees;

$\phi (T + \delta_1)$ = the pressure in atmospheres exerted by gaseous ammonia at $T + \delta^1$ degrees;

μ_3 = the weight of the gaseous ammonia above the liquid at $T + \delta^1$ degrees and corresponding pressure;

σ_3 = its specific heat at constant volume;

$\mu_3 \sigma_3$ = its value in water;

μ_4 = the weight of the mineral oil contained in $M - \mu_3$ grammes of liquid ammonia;

σ_4 = its specific heat;

$\mu_4 \sigma_4$ = its value in water;

μ_6 = the weight of the moisture contained in $M - \mu_3$ grammes of liquid ammonia;

$\varepsilon (\tau + \delta)$ = the specific heat of liquid ammonia at $\tau + \delta$ degrees;

$\phi (\tau + \delta)$ = the pressure in atmospheres exerted by gaseous ammonia at $\tau + \delta$ degrees;

μ_5 = the weight of the gaseous ammonia above the liquid at $\tau + \delta$ degrees and corresponding pressure;

$\mu_3 - \mu_5$ = the weight of the gaseous ammonia, which became a liquid when the temperature went down from $T + \delta_1$ to $\tau + \delta$ degrees;

r = the heat of evaporation of liquid ammonia in thermal units;

$(\mu_3 - \mu_5) r$ = thermal units developed by the liquefaction of $\mu_3 - \mu_5$ grammes of gaseous ammonia;

t = the temperature indicated by the thermometer in the water of the calorimeter at the beginning of the test;

τ = the temperature indicated by the thermometer in the water of the calorimeter at the end of the test;

δ = the fraction of a degree, which is to be added to τ, so as to obtain the temperature;

$\tau + \delta$ which the water in the calorimeter would have had, if no loss of heat had taken place by the cooling influence of air and by radiation;

$\tau + \delta - t$ = the corrected number of degrees by which the water in the calorimeter was heated up;

T = the temperature of the gaseous and liquid ammonia and its contaminations in the steel cylinder and of the cylinder itself, as indicated by the thermometer;

δ_1 = the fraction of a degree, which is to be added to T, so as to obtain the temperature;

$T + \delta_1$ which the thermometer would have indicated if its mercury column had not projected over the cover of the jacketed drum;

$T + \delta_1 - (\tau + \delta)$ = the decrease of temperature, which the gaseous and liquid ammonia and its contaminations in the steel cylinder and the cylinder itself underwent;

$\varkappa$ = the specific heat of liquid ammonia that is to be determined.

We have—

$$\varkappa = \frac{\begin{array}{l}(m + \mu\,\sigma + \mu_1\,\sigma_1)\,(\tau + \delta - t) - \\ (\mu_2\,\sigma_2 + \mu_3\,\sigma_3 + \mu_4\,\sigma_4 + \mu_6)\,(T + \delta_1 - (\tau + \delta)\,) - \\ (\mu_3 - \mu_5)\,r\end{array}}{(M - \mu_3 - \mu_4 - \mu_6)\,(T + \delta_1 - (\tau + \delta)\,)}$$

Authentical Proofs of the Determination of the Specific Heat of Liquid Ammonia.

	1.	2.	3.	4.	5.	6.	7.	8.
M,	128·3	128·1	128·1	128·1	128·1	128·0	128·0	128·0
$M-\mu_3-\mu_4-\mu_6$,	127·7516	127·5313	127·5276	127·5146	127·5237	127·4266	127·4262	127·4206
m,	980·0	These values are the same in all eight tests.						
μ,	216·2							
σ,	0·0939							
$\mu\sigma$,	20·30							
$\mu_1\sigma_1$,	6·37							
μ_2	1357·6							
σ_2,	0·117687							
$\mu_2\sigma_2$,	159·77							
v,	262·75							
μ_4,	0·071							
σ_4,	0·4618							
$\mu_4\sigma_4$,	0·033							
μ_6,	0·024							
r,	294·2							
$\varepsilon T+\delta_1$,	0·5470	0·5466	0·5471	0·5473	0·5462	0·5469	0·5457	0·5454
$\phi T+\delta_1$,	27·06	27·21	26·98	26·92	27·41	27·13	27·55	27·69
μ_3,	0·4734	0·4737	0·4774	0·4904	0·4813	0·4784	0·4788	0·4844
σ_3,	0·3606	0·3606	0 3606	0·3606	0·3606	0·3606	0·3606	0·3606
$\mu_3\sigma_3$,	0·1707	0·1718	0·1721	0·1769	0·1735	0·1795	0·1737	0·1747
$\varepsilon\tau+\delta$,	0·5895	0·5929	0·5926	0·5907	0.5965	0.5892	0.5886	0.5893
$\phi\tau+\delta$,	12·15	11·27	11·35	11·79	11·24	12·23	12·45	12·19
μ_5,	0·3317	0·3636	0·3624	0·3704	0·3854	0·3784	0·3833	0·3788
$\mu_3-\mu_5$,	0·1417	0·1101	0·1150	0·1200	0·0959	0·1000	0·0955	0·1056
$(\mu_3-\mu_5)\,r$,	41·68	32·66	33·83	35·30	28·21	29·42	28·10	31·06
t,	21·50°	18·25	18 64	20·40	18·00	21·83	22·20	21·39
τ,	31·15	28·71	28·93	30·28	28·67	31·42	32·00	31·38
δ,	0·139	0·092	0·09	0·114	0·054	0·119	0·073	0·095
$\tau+\delta$,	31·289	28·802	29·02	30·394	28·724	31·539	32·073	31·475
$\tau+\delta-t$,	9·789	10·552	10·38	9·994	10·724	9·709	9·873	10·085
T,	62·17	62·45	62·05	61·97	62.70	62·26	63·02	63·14
δ_1,	0·075	0·077	0·075	0·069	0·073	0·078	0·07	0·073
$T+\delta_1$,	62·245	62·527	62·125	62·039	62·773	62·338	63·09	63·213
$T+\delta_1-(\tau+\delta)$,	30·956	33·725	33·105	31·645	34·049	30·799	30·017	31·738
x,	1·22888	1·20757	1·21242	1·22941	1·22563	1·22720	1·25191	1·24707

Average of x, ... 1·22876

As this result was somewhat surprising, I wanted to make absolutely sure that no mistake had taken place in these tests; I therefore filled distilled water into the steel cylinder μ_2 and determined its specific heat. As I expected, I got a value close to one, namely 0·99302.

The values of μ_3 and μ_5 were calculated in the following manner; I take the figures obtained in the sixth test for example:

(1) $\mu_3 : T + \delta_1 = 62{\cdot}338^\circ$ $\varepsilon T + \delta_1 = 0{\cdot}5469$ $\phi T + \delta_1 = 27{\cdot}13$ atm.

$M = 128{\cdot}0$ grs. $v = 262{\cdot}75^{\mathrm{cm}}$ 1^{cm} of gaseous ammonia weighs at 0° and 760^{mm} pressure 0·0007614 grammes. Consequently, if the steel cylinder were entirely filled with liquid ammonia, its contents would weigh $262{\cdot}75 \times 0{\cdot}5469 = 143{\cdot}68$ grs. As they weigh only 128·0 grs., we have the following equation: $262{\cdot}75^{\mathrm{cm}} : 143{\cdot}68 \text{ grs.} = x^{\mathrm{cm}} : 128{\cdot}0 \text{ grs.}$ $x = 234{\cdot}04^{\mathrm{cm}}$ were filled with liquid ammonia. The rest $262{\cdot}75 - 234{\cdot}04 = 28{\cdot}71^{\mathrm{cm}}$ were filled with gaseous ammonia, which under the prevailing circumstances weigh

$$\frac{28{\cdot}71 \times 0{\cdot}0007614 \times 27{\cdot}13 \times 273}{273 + 62{\cdot}338} = 0{\cdot}4784 \text{ grs.}$$

(2) $\mu_5 : \tau + \delta = 31{\cdot}539^\circ$ $\varepsilon\tau + \delta = 0{\cdot}5892$ $\phi\tau + \delta = 12{\cdot}23$ atm. Doing the same calculations as above we obtain $x = 217{\cdot}43^{\mathrm{cm}}$, or $45{\cdot}32^{\mathrm{cm}}$ were filled with gaseous ammonia, which weigh 0·3784 grs.

II.—DETERMINATION OF THE TOTAL HEAT—HEAT OF EVAPORATION AND HEAT OF LIQUID OF AMMONIA.

In making this test I generally followed the course taken by H. V. Regnault (cf. *Ann. d. chim.*, xxiv, p. 375, pf.), but made the following two modifications:

(1) I introduced the value 1.22876 determined sub. I) for the specific heat of ammonia which Regnault supposed to be 0·799.

(2) I determined the value y_1 (cf. p. 476, pf.) which is necessary to be known for the calculation of the total heat and heat of liquid.

The test was made in the following way: The apparatus consists of two calorimeters *ABCD* and *EFGH*, which are filled in each test with 4,300 and 600 grs. of water respectively. Three tanks securely connected with each other by the brass-block *abcd* are put in the first calorimeter. Tank *IKL* is filled with the liquid ammonia *P*. During the test the ammonia gas escapes through the cock *Z* (the construction of which allows the regulation of the escape of the ammonia in the minutest manner) and the tanks *MNO* and *PQR* into tank *UVW*, put in the second calorimeter, and from it into the atmosphere. Small semi-circular plates are spirally fixed in these tanks so as to cause the gas to entirely equalize its temperature with that of the surrounding water. A small mercury manometer connected with *PQR* allows the control of the pressure of the escaping gas at any moment. By means of the agitator *y*, the temperature of the water is

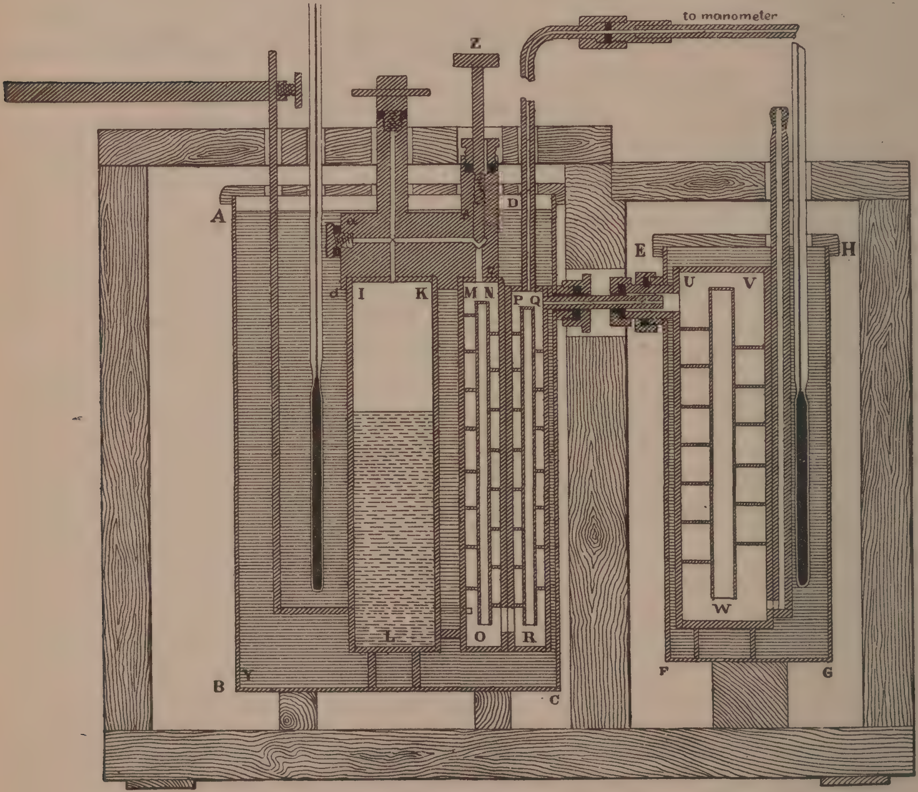

FIG. 1. Apparatus for the Determination of the Latent Heat of Ammonia.

kept the same in all strata. To lessen the influence of the air and to prevent the calorimeters as much as possible from radiating, the calorimeters are covered with wooden covers and the whole apparatus put in a wooden box.

The first calorimeter with its three tanks weighs 3,800 grs.; the second one 1,579 grs. The specific heat of their material (brass) being 0·0939 their values in water are 356·8 and 148·3 grs. respectively. Consequently the total weight of water (M) which is to be heated up in the first calorimeter is 4656·8 grs.; the total weight (M_1) in the second calorimeter 748·3 grs.

In this paper I shall always add to each item the figures obtained in the sixth test. What quantity P_1 (114·63 grs.) of the ammonia P (114·95) in tank IKL (capacity 242·05^{ccm}) was present in a liquid state, and what quantity $P - P_1$ (0·32) was present in a gaseous one, was calculated in the same way as μ_3 in I, p. 472.

If T is the temperature of the water in the first calorimeter at the commencement of the test (20°·69);

If T_1 is the temperature of the water in the first calorimeter at the end of the test (13°·82);

If $T_1 + \delta$ is the corrected temperature of the water in the first calorimeter at the end of the test (13°·5725);

If $T - (T_1 + \delta)$ is the number of degrees by which the water was cooled down (7°·1175);

If $\frac{T + T_1}{2}$ is the average temperature in the first calorimeter (17°·255);

If $\phi\, T$ is the tension of the ammonia vapor at $T°$ (6643$^{mm.}$);

If $\phi\, T_1$ is the tension of the ammonia vapor at $T_1°$ (5252$^{mm.}$);

If $\phi\, \frac{T + T_1}{2}$ is the average of both tensions (5947$^{mm.}$);

If τ is the temperature of the water in the second calorimeter at the commencement of the test (19°·11);

If τ_1 is the temperature of the water in the second calorimeter at the end of the test (18°·83);

If $\tau_1 + \delta_1$ is the corrected temperature of the water in the second calorimeter at the end of the test (18°·9816);

If $\tau - (\tau_1 + \delta_1)$ is the number of degrees by which the water was cooled down (0°·1284);

If $\frac{\tau + \tau_1}{2}$ is the average temperature in the second calorimeter (18°·97);

If ε is the mechanical equivalent of heat used under the prevailing circumstances by the gaseous ammonia for its expansion (317·4);

If c is the specific heat of gaseous ammonia (0·5084);

If C is the specific heat of liquid ammonia (1·22876).

The loss of heat, which both calorimeters together undergo, is

$$M\,[T - (T_1 + \delta)] + M_1\,[\tau - (\tau_1 + \delta_1)] = -\,33144{\cdot}8 - 96{\cdot}8$$
$$= -\,33241{\cdot}6 \text{ thermal units.}$$

But we have to make some corrections. There are to be subtracted:

(α) The quantity of heat s required by $P - P_1$ for changing its temperature from

$$T^\circ \text{ to } \tau^\circ;\ s = (P - P_1)\,c\,(T - \tau) = -\,0{\cdot}2$$

(β) The quantity of heat q_1 required by $P - P_1$ for expanding down to the atmosphere:

$$q_1 = \frac{10333\,(P - P_1)\,(273 + T)}{0{\cdot}7614\,.\,\varepsilon\,.\,273} = -\,9{\cdot}3$$

(γ) The quantity of heat s_1 required by P_1 for changing its temperature from

$$\frac{T + T_1}{2} \text{ to } \frac{\tau + \tau_1}{2}$$

after it had become a gas;

$$s_1 = P_1\,c\left(\frac{\tau + \tau_1}{2} - \frac{T + T_1}{2}\right) = -\,100{\cdot}0$$

There are to be added:

(δ) The quantity of heat s_2, which would have been required by P_1, if it had been filled into the tank *IKL* at

$$\frac{T+T_1}{2}; \quad s_2 = P_1\, C \left(T - \frac{T+T_1}{2}\right) = -387{\cdot}6$$

(ε) The quantity of heat q_2 required by P_1, in order to cool itself down to the temperature T_0, at which in reality it evaporates in tank *IKL*.

From the commencement of the evaporation, as soon as the gas begins to expand, the pressure prevailing in *IKL* ceases, being the one which corresponds to

$$\frac{T+T_1}{2} \text{ degrees,}$$

but it is lower. But if the pressure become lower, the temperature of evaporation must correspondingly become also lower, temperature and pressure of saturated vapor being dependent upon one another. Regnault, in determining the heat of evaporation of liquid carbonic acid, determined the decrease of temperature (y_1), which must be given to carbonic acid, in order to produce a cooling effect equal to the one produced, if it expands from a pressure of 1,000^{mm} above the atmosphere down to the atmosphere. This value y_1, not being known for ammonia, I determined it, entirely following the way used by Regnault, in determining y_1 for carbonic acid.

We first determine the decrease of temperature (y), which must be given to the unit of gaseous ammonia, in order to produce a cooling effect equal to the one produced if it expands from a pressure above the atmosphere ϕ down to the atmosphere, and from the so obtained value y we calculate the value y_1 for a pressure of 1,000^{mm} above the atmosphere.

Ammonia gas is developed in tank *A* (*Fig.* 2) and passes through the coils *FG* lying in the large tank *BCDE*, filled with water. At *a* the pipe enters the calorimeter *IKLM*. At *n*, the pipe of an inside diameter of 5^{mm} suddenly changes to a capillary tube, which at *o* changes again to a pipe of 5^{mm} diameter. An agitator in each tank keeps the temperature of the water equalized in all strata.

The ammonia, on entering the capillary tube at *n*, has the pressure corresponding to the temperature of the water in the large tank. On entering the wider tube at *o* and while passing through it, it expands down to the atmosphere. We admit that while passing through both tubes, the ammonia gas has the same temperature as the water in the calorimeter.

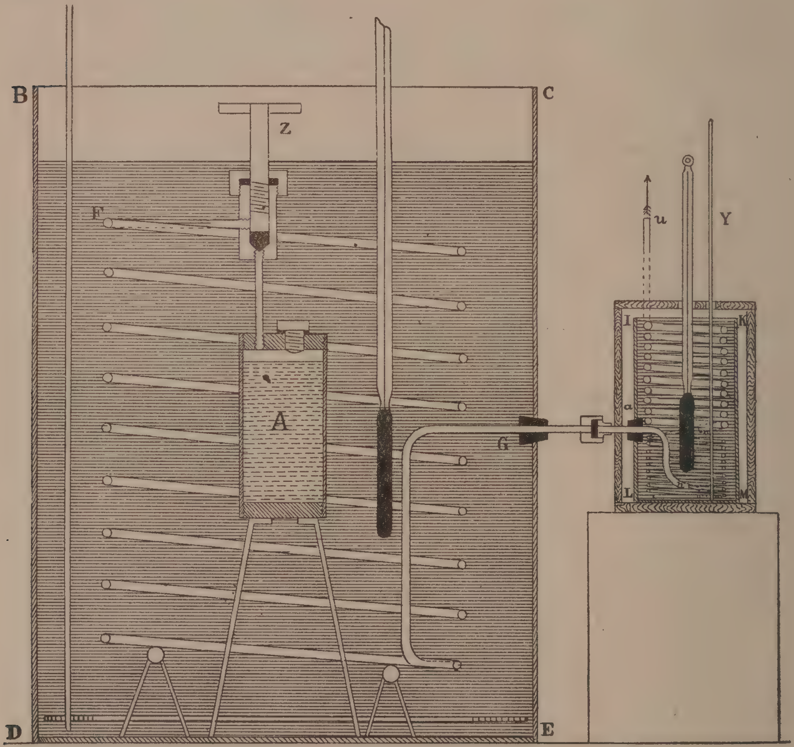

FIG. 2. Apparatus for the Determination of y_1.

If $M =$ the total quantity of water which is to be heated up, consisting in each test of 767 or 768 grs. of water and 104 grs. value in water of the tank;

$\phi =$ the pressure above the atmosphere expressed in mm. of mercury, at which the evaporation of ammonia takes place;

$\pi =$ the weight of the ammonia;

$\vartheta =$ the average temperature of the ammonia on entering the calorimeter;

ϑ_1 = the average temperature of the water in the calorimeter;

θ = the change of temperature which the water in the calorimeter underwent;

ω = the loss of heat caused by the ammonia by changing its pressure from ϕ to the atmosphere H;

c = the specific heat of gaseous ammonia = 0·5084.

We have:

The gaseous ammonia π entering the calorimeter at ϑ and leaving the same at ϑ_1, for doing so uses a quantity of heat $\pi\, c\, (\vartheta - \vartheta_1)$, its value being positive or negative, according to the value of $\vartheta >$ or $< \vartheta_1$. The quantity of heat taken from the calorimeter is $M\, \theta$. Consequently we have:

$$\omega + \pi\, c\, (\vartheta - \vartheta_1) = M\, \theta \text{ or } \omega = M\, \theta - \pi\, c\, (\vartheta - \vartheta_1).$$

From the definition given of y follows that

$$\omega = \pi\, c\, y \text{ or } y = \frac{\omega}{\pi\, c}$$

Introducing the above obtained value for ω into this equation, we have:

$$y = \frac{M\, \theta - \pi\, c\, (\vartheta - \vartheta_1)}{\pi\, c} \text{ and consequently as } y_1 = \frac{y \,.\, 1000}{\phi}$$

$$y_1 = \frac{[M\, \theta - \pi\, c\, (\vartheta - \vartheta_1)]\, 1000}{\pi\, c\, \phi}$$

The tests gave the following figures:

	1.	2.	3.	4.
ϕ,	5274·4 mm.	5259·2	5285·8	5441·6
π,	367·8 grs.	387·1	163·0	169·1
M,	871·0 grs.	871·0	872·0	872·0
ϑ,	18·563°	18·496	18·585	19·485
ϑ_1,	17·654°	14·996	19·325	18·871
$\vartheta - \vartheta_1$,	0·909°	3·500	— 0·840	0·614
θ,	— 1·538°	— 0·9887	— 0·7403	— 0·7303
$M\, \theta$,	— 1339·6 c.	— 861·2	— 645·3	— 636·6
$\pi\, c\, (\vartheta - \vartheta_1)$,	170·0 c.	688·8	— 69·6	52·7
ω,	— 1509·6 c.	— 1550·0	— 575·7	— 689·3
y,	— 8·07°	— 7·86	— 6·95	— 8·02
y_1,	— 1·530°	— 1·494	— 1·315	— 1·473

Taking the average, we obtain $y_1 = - 1^{\circ}.453$.

We return now to p. 476ε. Even now we are not able to determine the temperature T_0 directly, but we can determine the pressure (f) at which the ammonia in tank *IKL* evaporated and from it figure the corresponding temperature T_0.

The gas P, as well that developed by the liquid P_1 as the gaseous one $P - P_1$, expands from the unknown pressure f to the atmosphere H, for which it requires a quantity of heat q_0 expressed, according to the above said, by

$$\text{equation (1)}\ q_0 = P\,c\,y_1\,\frac{f - H^2}{1000}$$

The gas P, by its passing through the second calorimeter under the pressure H, takes $M_1(\tau - (\tau_1 + \delta_1))$ thermal units from it, during the same time changing its temperature from

$$\frac{T + T_1}{2} \text{ to } \frac{\tau + \tau_1}{2}$$

for which purpose

$$P\,c\left(\frac{T + T_1}{2} - \frac{\tau - \tau_1}{2}\right)$$

thermal units are required. If the gas P, on its entering the second calorimeter, had had the temperature

$$\frac{\tau + \tau_1}{2}$$

which it has on leaving the same, the heat required q_0 would be expressed by

$$\text{equation (2)}\ q_0 = M_1[\tau - (\tau + \delta_1)] + P_c\left(\frac{T + T_1}{2} - \frac{\tau + \tau_1}{2}\right)$$

Now, if the calculated average pressure

$$\phi\,\frac{T + T_1}{2}$$

be the real prevailing one,

$$\phi\,\frac{T + T_1}{2}$$

must be equal to f. Thus by putting the value obtained for

$$\phi \frac{T+T_1}{2}$$

in equation (1) for f and by figuring up both equations for q_0, we must, of course, obtain the same value for q_0 if our supposition

$$\phi \frac{T+T_1}{2}$$

to be equal to f be correct. Again, taking the figures obtained from the sixth test, we have

From equation (1) $q_0 = -433{\cdot}3$
From equation (2) $q_0 = -191{\cdot}1$

whence follows that f is not equal

$$\phi \frac{T+T_1}{2}$$

but smaller. If we introduce the value obtained from equation (2) for q_0 into equation (1) and figure it up for f we have

$$f = \frac{1000 \,.\, q_0}{y_1 \, P \,.\, c} + H = 3018^{\mathrm{mm}}$$

This was the real prevailing pressure at which the liquid in tank *IKL* evaporated.

The boiling point T_0, corresponding to this pressure, is $-0^\circ{\cdot}06$. Consequently we have—

$$q_2 = P\,C\left(\frac{T+T_1}{2} - T_0\right) = -2446{\cdot}1$$

Thus, the total heat (Q) required by the quantity of ammonia (P), at a certain temperature

$$\frac{T+T_1}{2}$$

is

$$Q = M[T-(T_1+\delta)] + M_1[\tau-(\tau_1+\delta_1)] - s - q$$
$$- s_1 + s_2 + q_2 = -35965{\cdot}8$$

or

The total heat (λ) required by the unit is

$$\frac{Q}{P} = -313{\cdot}7 \text{ thermal units.}$$

The heat of liquid (q) of the unit is

$$\frac{q_2}{P} = -\ 21{\cdot}3 \text{ thermal units.}$$

The heat of evaporation (r) of the unit is

$$\frac{Q - q_2}{P} = -\ 292{\cdot}4 \text{ thermal units.}$$

In the accompanying table, I give the figures obtained in the tests.

III.—DETERMINATION OF THE HEAT OF ABSORPTION OF AMMONIA.

The tests were made in the following way: The gas is developed by liquid ammonia contained in tank *AB* (*Fig. 3*). In order to have an as constant development of gas as possible during the test, tank *AB* is put in tank *CD* filled with water. Cock *Z* is of the same construction as cock *Z* in the preceding tests. The gas has to pass through the low stratum of mercury in the glass tube *EF*, and so its velocity can be controlled exactly. From hence the ammonia gas has to pass through the glass-coils *GH*. By passing through these coils lying in tank *IK*, the water of which is always renewed, the gas enters the absorption tank *NOPQ* at an almost constant temperature. The pipe *RS* reaches almost to the bottom of the tank and dips into a small glass tube secured in a piece of cork and filled with mercury, in order to prevent the water from rushing up in this pipe after it came in contact with the ammonia.

In each test 11,000 grammes of water are put in the absorption tank; its value in water being 245 grs., the weight of water (M) which is to be heated up is 11,245 grs. The quantity of ammonia gas (P) absorbed by the water is obtained by taking at the end of the test 100^{ccm} from the absorption tank, determining its contents of ammonia and multiplying the figure by 110.

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(*Strombeck.*)

AUTHENTICAL PROOFS OF THE DETERMINATION OF THE HEAT OF EVAPORATION, ETC., OF LIQUID AMMONIA.

	1.	2.	3.	4.	5.	6.	Average.
P,	31·39	55·83	116·05	116·4	115·3	114·95	
$P - P_1$,	1·04	0·92	0·29	0·30	0·32	0·32	
P_1,	30·35	54·91	115·76	116·10	114·98	114·63	
M,	4656·8	4656·8	4656·8	4656·8	4656·8	4656·8	
$\varphi\ T$,	5848	6506	6620	6313	6634	6643	
$\varphi\ T_1$,	5525	5848	5264	4983	5135	5252	
$\varphi\ \frac{T + T_1}{2}$	5686	6177	5942	5648	5885	5947	5863 mm. or 7·71 atm. abs. press.
f,	2524	3374	2732	2989	3365	3018	2987 mm. or 3·93 atm. abs. press.
T_o,	— 5·88	2·56	— 3·78	— 0·43	2·43	— 0·06	— 0·86° C. or 30°·45 F.
T,	17·19	20·13	20·64	19·30	20·68	20·69	
T_1,	15·20	16·60	13·70	12·31	13·74	13·82	
$T_1 + \delta$,	15·19	16·5143	13·3755	12·15536	13·40	13·5725	
$T - (T_1 + \delta)$,	— 2·00	— 3·6157	— 7·2645	— 7·14464	— 7·28	— 7·1175	
$\frac{T + T_1}{2}$	16·195	18·365	17·170	15·805	17·210	17·255	17°·00 C. or 62°·60 F.
$M\,[T - (T_1 + \delta)]$,	— 9313·6	— 16837·6	— 33829·3	— 33271·1	— 33901·5	— 33144·8	
ε,	317·4	317·4	317 4	317·4	317·4	317·4	
c,	0·5084	0·5084	0·5084	0·5084	0·5084	0·5084	
C,	1·22876	1·22876	1·22876	1·22876	1·22876	1·22876	
M_1,	748·3	748·3	748·3	748·3	748·3	748·3	
τ,	18·25	20·75	20·36	18·44	20·21	19·11	
τ_1,	18·13	20·55	20·17	18·43	20·08	18·83	
$\tau_1 + \delta_1$,	18·249	20·6882	20·2762	18·3849	20·13078	18·9816	
$\tau - (\tau_1 + \delta_1)$,	— 0·001	— 0·0618	— 0·0838	— 0·0551	— 0·07922	— 0·1284	
$M_1\,(\tau - [\tau_1 + \delta_1])$,	— 7·5	— 46·2	— 62·7	— 41·3	— 59·6	— 96·8	
$M_1\,[\tau - (\tau_1 + \delta)] + Pc\left(\frac{T + T_1}{2} - \frac{\tau + \tau_1}{2}\right)$	— 40·9	— 107·8	— 168·2	— 191·3	— 221·9	— 191·7	
$M\,[T - (T_1 + \delta)] + M_1\,[\tau - (\tau_1 + \delta_1),]$	— 9321·1	— 16883·8	— 33892·0	— 33312·4	33961·1	— 33241·6	
s,	— 0·6	— 0·3	— 1·0	— 0·1	— 0·04	— 0·2	
q_1,	— 47·2	— 40·6	— 13·0	— 13·5	— 14·4	— 9·3	
s_1,	— 30·8	— 63·1	— 181·7	— 153·2	— 169·6	— 100·0	
s_2,	— 29·7	— 95·3	— 394·3	— 399·5	— 391·4	— 387·6	
y'_1,	— 1·453	— 1·453	— 1·453	— 1·453	— 1·453	— 1·453	
q_2,	— 823·1	— 1339·2	— 2986·6	— 2322·2	— 2093 8	— 2446·1	
Q,	— 10095·3	— 18214·3	— 37077·2	— 35867·3	— 36262·3	— 35965·8	
$\lambda = Q/P$,	— 332·6	— 331·6	— 310·8	— 308·9	— 315·1	— 313·7	— 318·8 French or — 573·8 English cal.
$q = q_2/P_1$,	— 27·1	— 19·4	— 25·8	— 20·0	— 18·2	— 21·3	— 22·0 " — 39·6
$r = \frac{Q - q_2}{P_1}$	— 305·5	— 312·2	— 285·0	— 288·9	— 296·9	— 292·4	— 296·8 " — 534·2

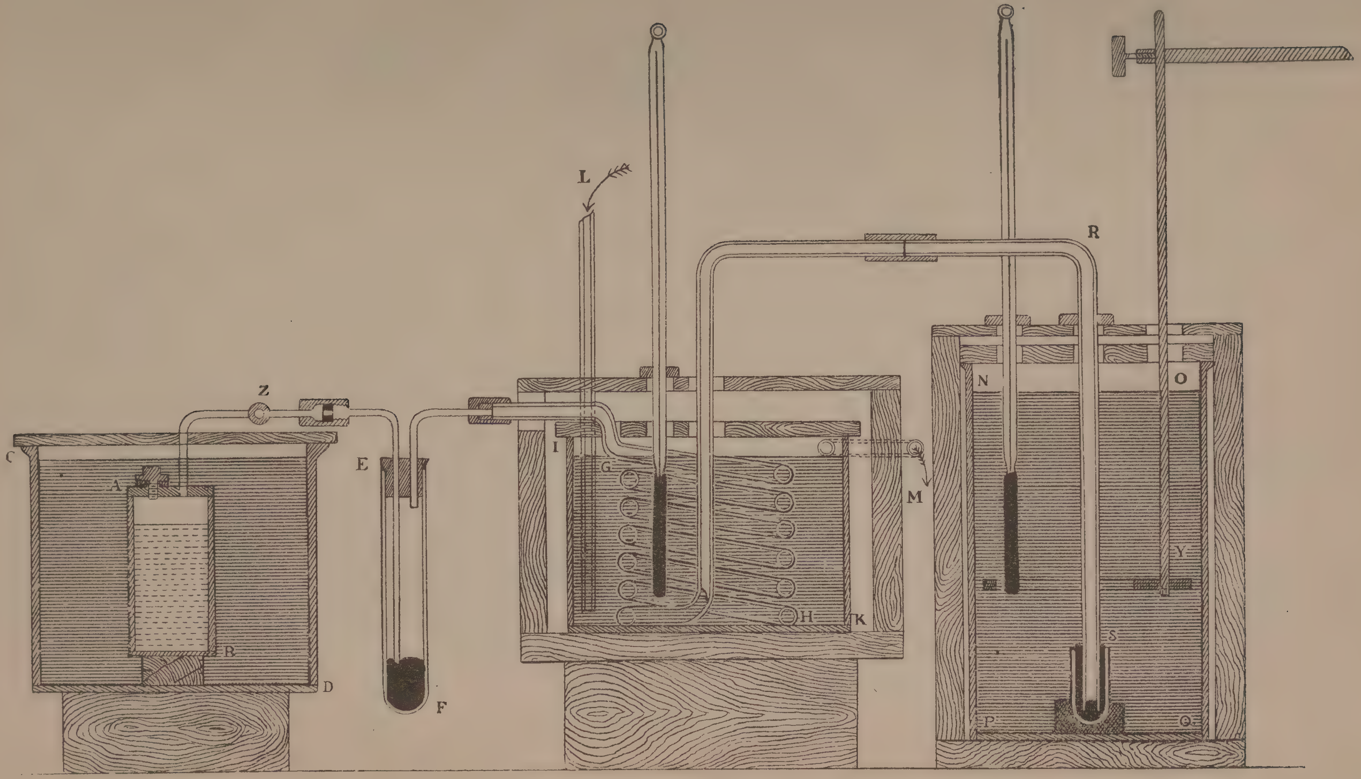


Fig. 3.—Apparatus for the determination of the heat of absorption of ammonia.

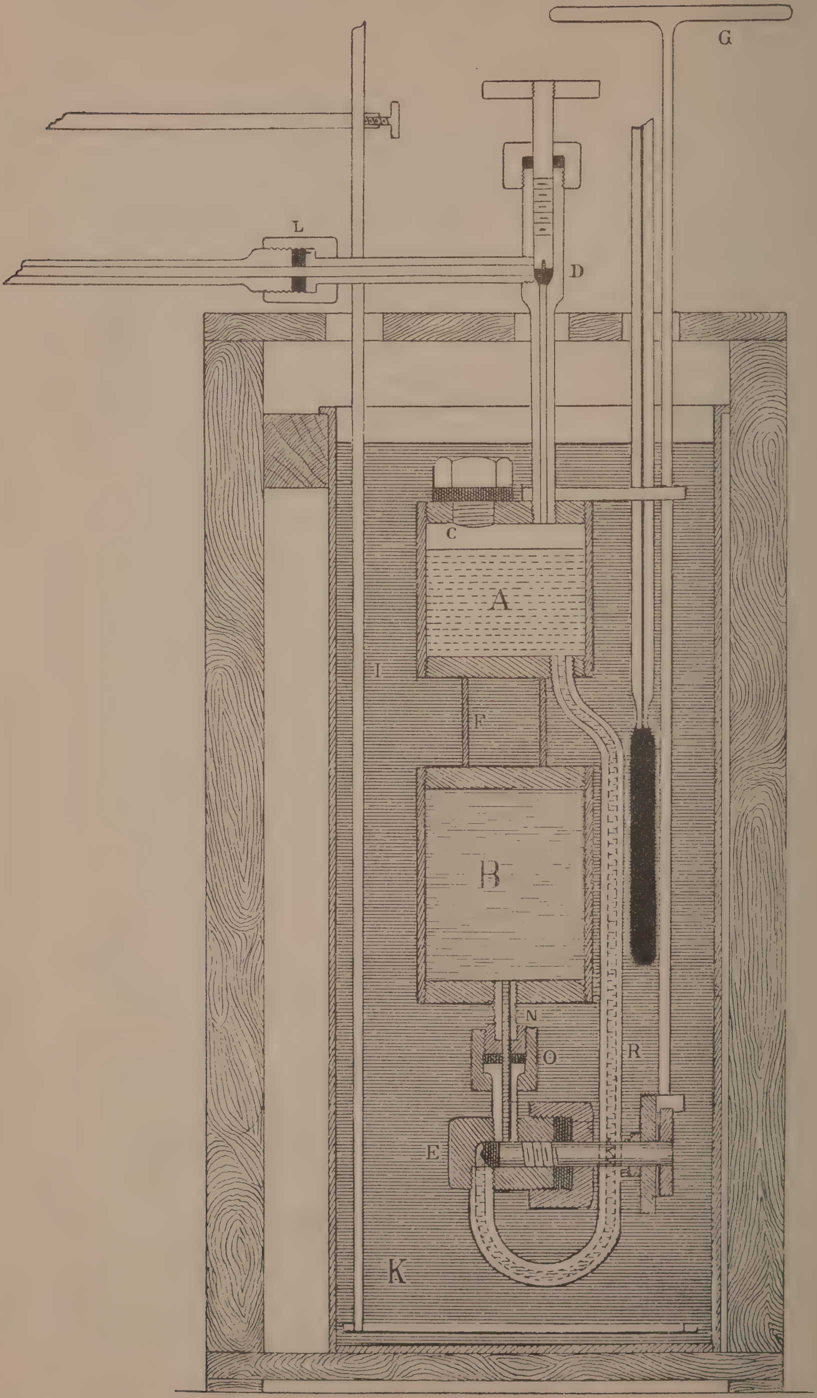


Fig. 4.—Apparatus for the determination of the heat of combination of ammonia.

I shall add to each item the figures obtained in the second test.

If in the following:

P is the weight of ammonia which was absorbed (108·67 grs.);

θ is the temperature of the water in the absorption tank at the commencement of the test (15°·88);

$\theta_1 + \delta$ is the corrected temperature of the water in the absorption tank at the end of the test (20°·79);

$\frac{\theta + \theta_1}{2}$ is the average temperature prevailing in the absorption tank during the test (17°·84);

$\frac{\tau + \tau_1}{2}$ is the average temperature of the ammonia on entering the absorption tank (17°·31);

$\frac{\theta + \theta_1}{2} - \frac{\tau + \tau_1}{2}$ is the difference of both temperatures (0°·53);

$\theta - (\theta_1 + \delta)$ is the number of degrees by which M was heated up (4°·88);

c is the specific heat of gaseous ammonia (0·5084).

The heat (Q) developed by P is

$$M\,[\theta - (\theta_1 + \delta)] = 54875{\cdot}6 \text{ thermal units.}$$

But we have to make one correction, it is to be added:

The quantity of heat (s) required by P for heating itself up from

$$\frac{\tau + \tau_1}{2} \text{ to } \frac{\theta + \theta_1}{2}; \; s = Pc\left(\frac{\theta + \theta_1}{2} - \frac{\tau + \tau_1}{2}\right) = 29{\cdot}3$$

Consequently we have

$$Q = 54875{\cdot}6 + 29{\cdot}3 = 54904{\cdot}9$$

or the heat developed by the unit (μ) is equal to

$$\frac{Q}{P} = 505{\cdot}3 \text{ thermal units.}$$

AUTHENTICAL PROOFS OF THE DETERMINATION OF THE HEAT OF ABSORPTION OF AMMONIA.

—	1.	2.	3.	4.	5.	6.	7.	8.	AVERAGE.
P,	112·25	108·67	110·1	148·5	134·0	100·54	152·2	170·5	
M,	11245·0	11245·0	11245·0	11245·0	11245·0	11245·0	11245·0	11245·0	
θ,	13·89	15·88	15·33	12·88	13·83	15·91	12·66	12·58	
$\theta_1 + \delta$,	19·20	20·79	20·31	19·68	20·06	20·61	19·80	20·65	
$\frac{\theta + \theta_1}{2}$	15·52	17·84	16·75	15·55	17·01	18·09	15·91	16·23	16°·61
$\frac{\tau + \tau_1}{2}$	14·693	17·31	15·59	14·96	15·85	16·06	15·27	16·00	
$\frac{\theta - \theta_1}{2} - \frac{\tau + \tau_1}{2}$	0·827	0·53	1·16	0·59	1·26	2·03	0·64	0·23	
$\theta - (\theta_1 + \delta)$,	5·175	4·88	4·7009	6·6315	5·944	4·5281	6·6704	7·4446	
$M(\theta - (\theta_1 + \delta))$,	58192·9	54875·6	55110·6	74571·2	66840·3	50918·5	75008·6	83714·5	
s,	47·3	29·3	66·3	46·1	87·7	104·1	47·7	18·6	
Q,	58241·4	54904·9	55177·9	74618·7	66928·6	51023·6	75057·7	83734·4	
$\mu = \frac{Q}{T}$	518·8	505·3	501·1	502·3	499·1	507·7	493·1	491·1	502·3 French or 904·1 Engl. thermal units

IV. DETERMINATION OF THE HEAT OF COMBINATION OF LIQUID AMMONIA AND WATER.

The tests were made in the following way: To tank A (*Fig. 4*) which through the hole c is to be filled with ammonia P is secured the pipe R, which has at its end the cock E and the union O; cock E can be handled by G. Union O can be connected with union N, terminating into the bottom of tank B, which is to be filled with water. Support F serves the purpose of making the whole apparatus steadier. I first made the connection between the upper ammonia- and the lower water-tank by a straight pipe going from the bottom of the upper to the top of the lower tank. In its middle a cock was placed which could be handled in the same way as the now present cock. But in this case at the place of contact between both fluids, a saturated stratum of aqueous ammonia is formed which, being heavier than liquid ammonia and lighter than water, does not move at all, but stays where it is, thus preventing both fluids from combining with one another. On the other hand, it will not do to put the liquid ammonia in the lower tank and the water in the upper one, for, it being next to impossible to fill a tank entirely with a fluid of such a low boiling point as liquid ammonia, there would always be left a small space filled with gaseous ammonia which, of course, would be at the top of the lower tank. Consequently, we would not determine the heat of combination but would again determine the heat of absorption.

In the following I shall add to each item the figures obtained in the first of the five tests I made.

Tank A is weighed empty, cocks E and D being closed, and L shut by a plug. Then it is filled with as much liquid ammonia as possible and weighed again. The difference between both weights is the one of ammonia P (53·7 grs.). At the end of each test it remains filled with ammonia gas ($P—P_1$) at atmospheric pressure. The contents of A being 160^{ccm}, $P—P_1$ weighs $160 \times 0·0007614 = 0·1218$ grs., which are to be subtracted from P, so as to obtain P_1 (53·58 grs.). After A is filled it and tank B are put in a large vessel with water, and after, by proper manipulations, B as well as the connecting pipe between A and B are entirely filled with water, both are connected. The whole apparatus being put in tank K filled with a certain quantity of distilled water, L is connected with a gauge after the plug is removed. The agitator I is put in motion, and the thermometer and the gauge are observed. As soon as for about five minutes the temperature and the pressure have become almost constant, cock E is opened. The pressure goes rapidly down to the atmosphere, and the thermometer ascends quickly, the temperature indicated by it soon becoming almost constant. From the figures thus obtained the heat of combining (ϕ) can be calculated.

The quantity of water (M) which is to be heated up in each test, consists of:

		grs.
The value in water of the apparatus, . . .		567·4
The weight of the water in tank B, . . .		237·0
The weight of the water in tank K, . . .		8200·0
The weight of the liquid ammonium in tank A, multiplied by its specific heat, . . .	$53{\cdot}58 \times 1{\cdot}22876 =$	65·8
	$M =$	9070·2

If

θ = the temperature of the water in tank K at the commencement of the test (20°·60);

θ_1 = the temperature of the water in tank K at the end of the test (21°·77);

$\theta - \theta_1$ = the difference between both temperatures (1·170);

p^{θ} = the absolute pressure in atmospheres prevailing at the commencement of the test (8·69);

p^{θ_1} = the absolute pressure in atmospheres prevailing at the end of the test (1·0);

the heat developed by the combining of P_1 (53·58 grs.) with water is equal to $M\ (\theta - \theta_1) = 10612{\cdot}1$ or the heat (ϕ) developed by the unit is

$$\phi = \frac{M\ (\theta - \theta_1)}{P_1} = 198{\cdot}1 \text{ thermal units.}$$

I did not take into consideration the difference of weight between the few cubic centimeters of gaseous ammonia being over the liquid at the commencement of the test at p^{θ} and the 160^{ccm} of gaseous ammonia filling tank A at the end of the test at p^{θ_1}, because its influence on the result, if any, can only be minimal.

According to the equivalents of NH_3, H_2O, 17 grs. of the former combine with 18 grs. of the latter to 35 grs. of $NH_4(OH)$. Therefore, from a theoretical point of view, it would be best to use ammonia and water in these proportions in a test. But, because of technical reasons, the surface of contact between ammonia and water in an apparatus can be only small, so that the diffusion between both will take place rather quickly only then if the specific gravity of the resulting aqueous ammonia is a great deal greater than the one of liquid ammonia; for in this case there is always in B a descending current of aqueous ammonia and an ascending current of liquid ammonia, and fresh water comes always into contact with fresh ammonia. I, therefore, took the dimensions of tanks A and B in such a way that the ratio between the combining ammonia and water was, instead of 17 : 18, only about 8 : 18.

The results obtained in the other four tests were :

	2.	3.	4.	5.	Average of all 5 tests.
P, ...	59·2 grs.	60·22	55·12	60·20	
P_1, ...	59·08 grs.	60·10	55·00	60·08	
$P - P$, ...	0·12 grs.	0·12	0·12	0·12	
M, ...	9276·5 grs.	9277·7	9271·1	9277·7	
θ, ...	21°·29	23°·94	19°·62	21°·16	
θ_1, ...	22°·48	25°·29	20°·84	22°·47	
$\theta - \theta_1$, ...	1°·19	1°·35	1°·22	1°·31	
$M(\theta - \theta_1)$, ...	11039·0	12524·9	11310·7	12153·9	
p^{θ}, ...	8·75 atm.	9·68	8·39	8·52	
p^{θ_1}, ...	1	1	1	1	
ϕ, ...	186·9	208·4	205·6	202·3	{ 200·3 French or 360·5 Eng. thermal units.

V. TABLE, *Showing the amount in French and English thermal units required or developed by liquid or gaseous ammonia when changing their respective states of aggregate and for what these thermal units are used.*

Total heat required by liquid ammonia to transform itself at 17°·0 (62°·60 F.) into saturated vapor, its boiling point being in reality at — 0°·86 (30°·45 F.), ...	— 318·8 (573.8)	— 296·8 (534·2)	heat of evaporation.
		— 22·0 (39·6)	heat of liquid.
Heat developed by the absorption of gaseous ammonia by water at atmospheric pressure, the temperature of the resulting aqueous ammonia being 16°·6 (61°·9 F.), .	+ 502·3 (904·1)	+ 318·8 (573·8)	to become a liquid at — 0°·86.
		+ 46·2 (83·2)	to cool itself down from — 0·86° to its boiling point at atmospheric pressure to — 38°·5 = 37 64 × 1·22876.
		— 67·6 (121·7)	to heat itself up from — 38°·5 to 16°·6 = 55·1 × 1·22876.
		+ 200·3 (360·5)	for chemical work done by the combination of liquid ammonia and water.
		+ 497·7 (895·8)	

PROCEEDINGS.

[*Stated meeting, held at the institute, Tuesday, December 16, 1890.*]

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, December 16, 1890.

Mr. T. C. Palmer, president, in the chair.

Members present: Prof. E. F. Smith, Prof. L. B. Hall, Dr. Wm. H. Wahl, Mr. Lee K. Frankel, Mr. H. Pemberton, Jr., Mr. Reuben Haines, Dr. S. C. Hooker, Prof. Henry Trimble, and several visitors.

Dr. Wahl, as chairman of the committee to prepare a circular to be addressed to the chemists of the country, reported progress, and the committee was continued. The secretary read his annual report to the section, which was accepted.

The election of officers followed, and, on motion, it was decided that the secretary cast the vote of the section for the ticket nominated at the November meeting. Dr. Wahl was escorted to the chair by the retiring president, and, on taking his seat, made a brief address appropriate to the occasion.

On motion of Dr. Hall, it was voted that the officers, president, secretary and treasurer, constitute three of the seven members of the committee on admissions.

The following gentlemen were then nominated and elected to fill the remaining vacancies in the committee, viz: Mr. H. Pemberton, Jr., Dr. S. E. Hooker, Prof. E. F. Smith, Dr. L. B. Hall.

The president appointed Messrs. Haines and Frankel to act with the secretary as members of the finance committee.

Dr. Wahl referred to the approaching convention of chemists, to be held shortly in this city, stating what had been done by the local committee to arrange for the event, and expressed the wish that the members of the section would second the efforts of the local committee to make the visitors welcome.

Dr. Greene exhibited specimens of the alloys of sodium and lead, discussed in the paper by himself and Dr. Wahl at the last meeting. They were examined with much interest.

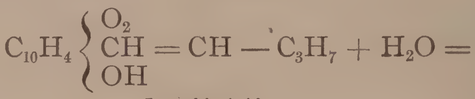
Adjourned. WM. C. DAY, *Secretary.*

ON SOME DERIVATIVES OF LAPACHIC ACID.

By SAMUEL C. HOOKER and WM. H. GREENE.

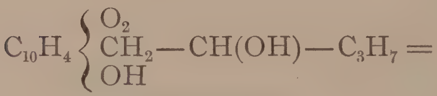
[*Read before the Chemical Section, March 18, 1890.*]

In a preliminary paper* published by the authors, it was shown that the conversion of lapachic acid into lapachone,† by the action of strong mineral acids, probably occurs in two stages, as indicated in the following equations:



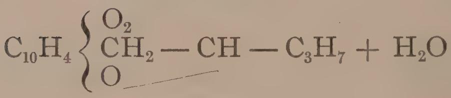
$$C_{10}H_4\left\{\begin{matrix}O_2\\CH=CH-C_3H_7\\OH\end{matrix}\right. + H_2O =$$

Lapachic Acid.



$$C_{10}H_4\left\{\begin{matrix}O_2\\CH_2-CH(OH)-C_3H_7\\OH\end{matrix}\right. =$$

Oxyhydrolapachic Acid.



$$C_{10}H_4\left\{\begin{matrix}O_2\\CH_2-CH-C_3H_7\\O\end{matrix}\right. + H_2O$$

Lapachone.

In support of this view it was stated that lapachone can be readily converted into oxyhydrolapachic acid, and that this acid, under the influence of mineral acids, again readily passes into its anhydride lapachone.

The details of these experiments, which have not yet been printed, will be published in this paper.

CONVERSION OF LAPACHONE INTO OXYHYDROLAPACHIC ACID.

The action of aqueous potash on lapachone has been studied by Paterno,‡ who writes as follows: "In aqueous potash of medium concentration lapachone does not dissolve in the cold; on heating it passes into a fine purple-red solution which, filtered while hot, deposits on cooling beautiful orange needles of silky lustre, recognized by their fusing point (154°–155°) to be lapachone. On the addition of hydrochloric acid the alkaline filtrate yields a precipitate, which, purified by recrystallization, was similarly found to be lapachone."

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* This *Journal*, **128,** 142.

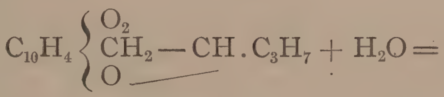
† *Gazz. chim. Ital.*, **12,** 372.

‡ *Gazz. chim. Ital.*, **12,** 372.

This statement is misleading. The facts are these: Lapachone dissolves with some difficulty in hot aqueous potash, but in so doing undergoes a change. A new compound, an acid, is formed, and this, and not lapachone, exists in the solution obtained. If hydrochloric acid, in very slight excess, be added to the cold alkaline solution, the new compound separates as a yellow oil, which gradually assumes a crystalline form. If, however, a larger quantity of hydrochloric acid be employed, the color of the turbid solution is seen gradually to change. The bright yellow gives place to orange, and finally red crystals of lapachone may be observed floating in the liquid.

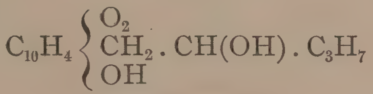
The new compound has, in fact, been reconverted, by the excess of hydrochloric acid employed, into lapachone. The experiment has been repeated a number of times, but the authors have not once observed the separation of crystals of lapachone from the alkaline solution as described by Paterno.

The action of potash on lapachone is shown in the following equation:



$$C_{10}H_4\left\{\begin{array}{l}O_2\\ CH_2-CH\,.\,C_3H_7\\ O\end{array}\right. + H_2O =$$

Lapachone.



$$C_{10}H_4\left\{\begin{array}{l}O_2\\ CH_2\,.\,CH(OH)\,.\,C_3H_7\\ OH\end{array}\right.$$

Oxyhydrolapachic Acid.

In order to prepare oxyhydrolapachic acid, eight grams of lapachone, four grams of caustic potash and 150 cc. of water are heated together. If the crystals of lapachone be large, they should be first powdered. As the lapachone is dissolved, the color of the solution becomes very intense, being similar to that of the salts of lapachic acid.

After boiling several minutes, the solution is filtered to remove any crystals which may have escaped the action of the potash, and an excess of acetic acid is then added. A yellow oil is immediately precipitated, which collects in the bottom of beaker, and then appears considerably darker than when first seen in a fine state of division. In the course of an hour or so, it solidifies to a yellow crystalline mass which, after some hours, may be separated and washed well with water. The acid, as thus obtained, though slightly colored at the surface, is in a very pure condition and can be rendered absolutely so by crystallization once or twice from alcohol, in which it dissolves very readily and from which it separates slowly in monosymmetric crystals. The yield is theoretical; eight grams of lapachone gave 8·4 grams of the crude acid; that required by theory being 8·59 grams.

The following figures were obtained on analysis:

(I) ·1965 gram gave ·4970 CO_2 and — H_2O
(II) ·4932 " " 1·2510 CO_2 " ·2743 H_2O
(III) ·2093 " " ·5306 CO_2 " ·1160 H_2O

	Found. I.	II.	III.	Calculated for $C_{15}H_{16}O_4$.
C, ...	68·96	69·18	69·13	69·23
H, ...	lost	6·18	6·15	6·15

Oxyhydrolapachic acid melts at 125°. It is readily soluble in most of the ordinary solvents, from which it crystallizes after standing some time; if, however, the solvent be allowed to evaporate rapidly, the acid is left as a yellow oil. Under ordinary conditions it is a perfectly stable body, which can be crystallized from acetic acid unchanged; but in contact with mineral acids, even when dilute, it is readily converted into its anhydride lapachone, which was identified by its fusing point and other properties, and by analysis.

The barium salt is extremely characteristic, separating from a claret-colored solution in bright *orange*, silk-like needles, grouped together in wavy tufts. In order to prepare it, the acid was dissolved in a solution of baric hydrate, from which the excess of barium was precipitated at the boiling temperature by means of carbon dioxide. The solution was then concentrated to the crystallizing point. As the evaporation proceeds, a film of the salt, in an amorphous condition, and of the *same* color as the solution, forms at the edge of the liquid, on the evaporating basin. The salt is much more soluble in hot than in cold water. After recrystallization, the orange needles gave the following figures on analysis:

(I) ·2152 gram substance gave ·0744 $BaSO_4$.
(II) ·2883 " " " ·0987 "
(III) ·2478 " " " ·0854 "

	Found.			*Calculated for*	
	I.	*II.*	*III.*	$(C_{15}H_{15}O_4)_2Ba, H_2O$.	$(C_{15}H_{15}O_4)_2Ba$.
Ba (per cent.), .	20·32	20·12	20·26	20·35	20·91

The above figures were obtained from different preparations, dried over sulphuric acid, and also at 110°.

The salt evidently contains one molecule of water of crystallization, although the attempts to determine this by loss were unsuccessful. Heated to 110° for several hours, no change in weight occurred, and decomposition commenced at somewhat higher temperatures. It was, however, observed that the orange crystals, when rubbed, became dark magenta-red, and analysis proved the altered salt, dried at 105°–110°, to be anhydrous. Under the microscope, it showed no definite structure, and when moistened with water it became immediately orange, at the same time swelling up and then passing into solution. On evaporation, the characteristic orange needles of the salt, as above described, were again obtained.

The anhydrous salt was prepared for analysis by thoroughly grinding the orange crystals, in small quantities at a time, in an agate mortar. The conversion was not easily accomplished, and it seemed as if a resinous substance were being dealt with. The ground substance was heated to 110° until constant in weight.

(I) ·3368 gram substance gave ·1182 $BaSO_4$.
(II) ·2834 " " " ·1002 "

	Found.		*Calculated for*
	I.	*II.*	$(C_{15}H_{15}O_4)_2Ba$.
Ba., ...	20·63 p.c.	20·78 p.c.	20·91 p.c.

The two determinations were made with different preparations.

The calcium salt is entirely different from the barium salt just described. It separates from its solution on evaporation in small dark-red crystals, and is only very sparingly soluble in both hot and cold water. After drying over sulphuric acid, it did not lose in weight when exposed for over an hour to a temperature of 105°–110°. Analysis shows it to be anhydrous.

(I) ·3113 gram gave ·0808 $CaSO_4$
(II) ·2594 " " ·0635 "

	Found.		Calculated for
	I.	II.	$(C_{15}H_{15}O_4)_2Ca$.
Ca., ...	7·63 p.c.	7·19 p.c.	7·16 p.c.

The preparations analyzed were different. (I) was obtained by adding the theoretical quantity of calcium chloride to the slightly ammoniacal solution of the acid; on expelling the excess of ammonia by heat, the salt separated. (II) was prepared as above described for orange variety of the barium salt.

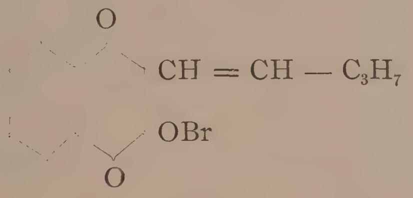
The silver salt was obtained by precipitating a concentrated neutral solution of the ammonium salt with the calculated quantity of silver nitrate. It separates in a semi-resinous condition, becoming granular after some time. It is decidedly soluble in water, also in dilute alcohol, from which it separates, on spontaneous evaporation, in small dark-red needles. The figures it gave on analysis lie between those required for $C_{15}H_{15}O_4Ag$ and $C_{15}H_{15}O_4Ag + H_2O$. It is probable, therefore, that the compound was not obtained in a pure condition.

ON SOME DERIVATIVES OF LAPACHIC ACID.

BY SAMUEL C. HOOKER.

[*Read before the Chemical Section, Franklin Institute, May 20, 1890.*]

Through the action of bromine on lapachic acid in acetic acid solution, Paterno* obtained a compound $C_{15}H_{13}BrO_3$, which he regarded as bromlapachic acid, and in which he believed the bromine to have replaced the hydroxylic hydrogen of lapachic acid. He, therefore, assigned to it the formula†



In selecting this formula, Paterno was guided by the following reactions:

(1) Lapachic acid dissolves readily in alkalies in the cold, but bromlapachic acid does not.

(2) The monacetyl derivative of lapachic acid yields on treatment with bromine bromlapachic acid.

(3) On oxidation with nitric acid phthalic acid, not bromphthalic acid, is formed.

(4) Unlike lapachic acid, bromlapachic acid undergoes no changes in contact with concentrated sulphuric acid.

In view of the light thrown on the formation of lapachone from lapachic acid by the author in conjunction with Dr. Wm. H. Greene,‡ it seems probable that the action of bromine on lapachic acid takes place as indicated in the following equations, and that the resulting compound is bromlapachone, and not bromlapachic acid.

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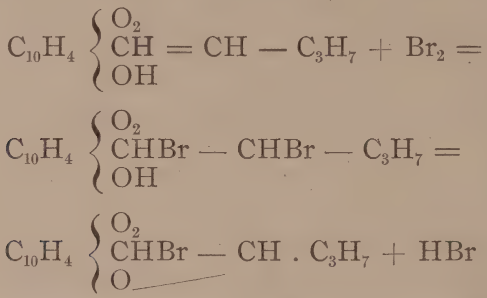
* *Gazz. chim. Ital.*, **12**, 353.

† It still remains an open question whether lapachic acid is derived from α- or β-napthaquinone. Paterno is occupied in solving this question. See also preceding paper.

‡ This *Journal*, **128**, 147.



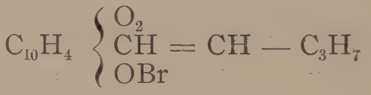
$$\mathrm{C_{10}H_4} \left\{ \begin{array}{l} \mathrm{O_2} \\ \mathrm{CH = CH - C_3H_7 + Br_2 =} \\ \mathrm{OH} \end{array} \right.$$

$$\mathrm{C_{10}H_4} \left\{ \begin{array}{l} \mathrm{O_2} \\ \mathrm{CHBr - CHBr - C_3H_7 =} \\ \mathrm{OH} \end{array} \right.$$

$$\mathrm{C_{10}H_4} \left\{ \begin{array}{l} \mathrm{O_2} \\ \mathrm{CHBr - CH\,.\,C_3H_7 + HBr} \\ \mathrm{O} \end{array} \right.$$

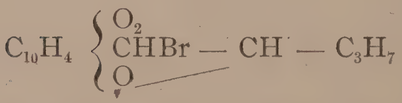
This view was advanced by Hooker and Greene* about a year ago, without, however, being supported by direct experimental evidence. It was afterwards discussed by Paterno and Minunni† who, although admitting it had some strong points in its favor, did not appear to regard it on the whole as probable.

In order to distinguish between the formulæ



$$\mathrm{C_{10}H_4} \left\{ \begin{array}{l} \mathrm{O_2} \\ \mathrm{CH = CH - C_3H_7} \\ \mathrm{OBr} \end{array} \right. \qquad (1)$$

and



$$\mathrm{C_{10}H_4} \left\{ \begin{array}{l} \mathrm{O_2} \\ \mathrm{CHBr - CH - C_3H_7} \\ \mathrm{O} \end{array} \right. \qquad (2)$$

the action of potash on the so-called bromlapachic acid has been studied, as it seemed probable that, if its constitution is correctly represented by the formula (1), lapachic acid would be again formed by the removal of the bromine. If, on the other hand, the compound is a derivative of lapachone it should behave similarly to lapachone (see preceding paper) in contact with potash.

The results obtained prove unmistakably that Paterno's so-called monobromlapachic acid is in reality monobromlapachone.

The action of dilute potash upon the compound at the boiling temperature is represented in the following equation:

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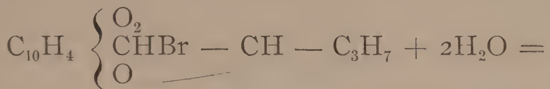
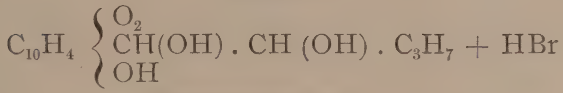
* This *Journal*, **128**, 147.

† *Gazz. chim. Ital.*, **19**, 623.



$$C_{10}H_4\left\{\begin{array}{l}O_2\\ CHBr - CH - C_3H_7 + 2H_2O =\\ O\end{array}\right.$$

Bromlapachone.

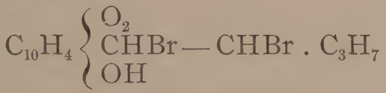


$$C_{10}H_4\left\{\begin{array}{l}O_2\\ CH(OH) . CH (OH) . C_3H_7 + HBr\\ OH\end{array}\right.$$

Dioxyhydrolapachic Acid.

If bromlapachone had the formula which Paterno assigns to it as bromlapachic acid, it should form an addition compound with bromine. The author has allowed it to remain for several days in contact with the theoretical quantity of bromine in chloroform solution, but has not observed the formation of any addition compound. Bromlapachone was recovered unchanged.

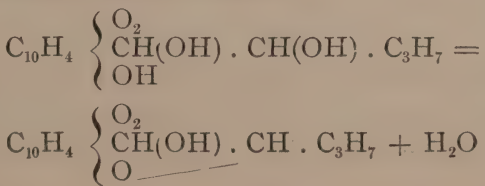
In order to remove all doubts as to the mechanism of the reaction resulting in the formation of bromlapachone, the study of the action of bromine on lapachic acid in chloroform solution has been undertaken in the hope of isolating the intermediate product



$$C_{10}H_4\left\{\begin{array}{l}O_2\\ CHBr—CHBr . C_3H_7\\ OH\end{array}\right.$$

In the course of this investigation no less than five compounds have been obtained by the action of one molecule of bromine on one molecule of lapachic acid. The study of these interesting bodies has had to be temporarily suspended, owing to dearth of material, but it is hoped that the work will be soon resumed and the results soon ready for publication.

By the action of dilute mineral acids upon dioxyhydrolapachic acid it is converted with great ease into its anhydride, oxylapachone, as follows:



$$C_{10}H_4\left\{\begin{array}{l}O_2\\ CH(OH) . CH(OH) . C_3H_7 =\\ OH\end{array}\right.$$

$$C_{10}H_4\left\{\begin{array}{l}O_2\\ CH(OH) . CH . C_3H_7 + H_2O\\ O\end{array}\right.$$

Further, just as oxyhydrolapachic acid results from the action of alkalies on lapachone, so dioxyhydrolapachic acid results from their action on oxylapachone.

BROMLAPACHONE.

In the course of some experiments, already referred to, it was observed that, under certain conditions, bromlapachone (Paterno's monobromlapachic acid) could be readily obtained by the action of bromine on lapachic acid in chloroform solution. As the yield is much larger and the substance purer than when prepared in acetic acid solution, as described by Paterno, this method of preparation was employed. It will be described in detail when the compounds arising from the action of bromine on lapachic acid in chloroform solution are discussed.

The bromlapachone was first carefully compared with that prepared as directed by Paterno, and in all particulars was found to be identical. A bromine estimation was made, with the following result:

·2588 grm. substance gave ·1502 AgBr.

	Found.	*Calculated for* $C_{15}H_{13}BrO_3$.
Br, ...	24·69	24·92

Bromlapachone has been observed by Paterno to separate from its solution in alcohol in orange-red crystalline plates. While able to confirm this observation, the author has also obtained it, when in a pure form, crystallized in tufts of fine needles. The conditions under which both varieties of crystals are formed may be stated generally as follows:

From slightly impure alcoholic solutions bromlapachone separates in plates. The same is true whether the solution be allowed to remain at perfect rest, or be disturbed while crystallization is proceeding.

From pure concentrated solutions bromlapachone can be readily obtained in plates by keeping the solution slightly in motion while the compound is crystallizing out.

If the compound, crystallized in plates and still in contact with its saturated mother liquor, be allowed to stand one or more weeks, the plates will be gradually replaced by tufts of needles. This change is believed to occur only when the compound is in a very pure condition. The observation was first accidentally made, and the experiment was then repeated several times.

Pure solutions protected from dust and allowed to stand absolutely at rest frequently deposit the compound crystallized entirely in tufts of needles.

By observing only partially the above conditions both varieties of crystals may often be obtained in some solution.

The above remarks apply to all solutions of bromlapachone, whether obtained from needles or plates.

The melting points of the two varieties of crystals differ only very slightly, if at all. That of the plates was found to be 138°·5; that of the needles, 138°.

A combustion of the needles gave the following results:

·2399 grm. substance gave ·4932 CO_2 and ·0870 H_2O.

	Found.	*Calculated for* $C_{15}H_{13}BrO_3$
C, ...	56·06	56·07
H, ...	4·02	4·04

CONVERSION OF BROMLAPACHONE INTO DIOXYHYDROLAPACHIC ACID.

As the result of several experiments 1·5 grams of finely-powdered bromlapachone and 75 cc. of a one per cent. solution of caustic potash were boiled together with an inverted condenser. The bromlapachone dissolved slowly to an intense carmine-red solution. At the end of fifteen minutes the boiling was discontinued and the solution filtered. Stray crystals of bromlapachone, which had escaped grinding and were consequently able to resist the action of the potash for a long time, were thus removed. It was observed that a small quantity of a green substance, formed by the action of the potash, was also retained on the filter paper. A slight excess of acetic acid was added to the filtered solution when cold, resulting in the immediate formation of a precipitate in small quantity, consisting of a somewhat resinous brown substance. This was removed as quickly as possible by filtration through a folded paper of comparatively large size. The filtration must be promptly accomplished, otherwise the new acid will commence to crystallize out before the separation of the brown impurity has been effected. In a very minutes after acidifying the acid commences to be deposited from the now orange-red solution in compact crystalline grains. The separation occurs slowly, the solution becoming simultaneously lighter in color. In the course of a few hours the crystallization is complete and the compound can be filtered off, washed well with water and dried. The acid, as thus obtained, is almost pure: 1·5 grams bromlapachone gave rather more than one gram of the new acid. It was twice recrystallized from ninety-five per cent. alcohol, in which it is not very soluble, and analyzed. A qualitative test showed that in spite of the diluteness of the potash solution used the bromine had been removed.

·1867 gram gave ·4442 CO_2 + ·0989 H_2O.

	Found.	*Calculated for* $C_{15}H_{16}O_5$.
C, ...	64·88	65·21
H, ...	5·88	5·79

Dioxyhydrolapachic acid melts at 181°–182°. Like bromlapachone, it crystallizes from ninety-five per cent. alcohol in two apparently different forms. No special experiments were made to determine the conditions governing the formation of each variety of crystal and sometimes the one form, sometimes the other, would be obtained under apparently similar conditions. One modification (that analyzed) consists of small prismatic crystals, often grouped together in the form of compact stars; the other, of very fine long needles, crystallizing in tufts.

This acid, like oxyhydrolapachic and lapachic acids, forms stable salts which are not decomposed by carbon dioxide. The color of their solutions is similar to that of those of lapachic acid. The small amount of available material did not permit a more complete study of these salts. Dioxyhydrolapachic acid dissolves somewhat in water and is soluble in all ordinary solvents.

CONVERSION OF DIOXYHYDROLAPACHIC ACID INTO OXYLAPACHONE.

While dioxyhydrolapachic acid is perfectly stable under ordinary conditions and shows no inclination whatever to pass into its anhydride, it forms oxylapachone with great readiness in contact with mineral acids.

To a solution of 1·36 grams of the acid * in the smallest possible quantity of boiling 95 per cent. alcohol, 5 cc. of concentrated hydrochloric acid were added: the color of the solution changed to an intense orange-red. After boiling for one or two minutes the solution was diluted with water as long as a precipitate was produced. A considerable portion of the oxylapachone was thus precipitated in small orange-red needles. The filtrate, still orange in color, was evaporated until a crust of crystals had formed on its surface. They were separated from the solution when cool. Total yield, 1·15 grams. The substance was purified for analysis by recrystallization from dilute alcohol; it separated in red needles, fusing at 201°·5, and closely resembling lapachone in appearance.

·2507 gram gave ·6401 CO_2 + ·1228 H_2O.

	Found.	*Calculated for* $C_{15}H_{14}O_4$.
C,	69·63	69·76
H,	5·44	5·42

CONVERSION OF OXYLAPACHONE INTO DIOXYHYDROLAPACHIC ACID.

Oxylapachone, like lapachone and bromlapachone, is almost insoluble in alkalies in the cold; on boiling, however, it readily passes into solution. Thirty-five cc. of a one per cent. solution of caustic potash, and 1·35 grams oxylapachone, were heated for several minutes at the boiling point. The solution was then filtered, cooled and acidified with acetic acid. Crystals commenced to form almost immediately, but the separation was not complete for some hours. After crystallization from alcohol the compound fused at 181°–182°, and in other respects was found to be identical with dioxyhydrolapachic acid, obtained as above-described from bromlapachone. The yield of the crude substance was almost theoretical; 1·35 grams gave 1·36 grams of the acid, 1·45 being required by theory.

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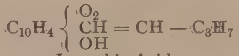
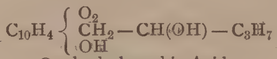
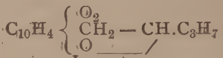
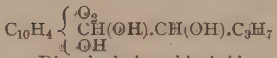
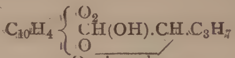
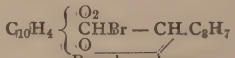
* The whole of the substance available after a few preliminary experiments had been made on a still smaller scale.

·1834 gram gave ·4390 CO_2 + ·0958 H_2O.

	Found.	Calculated for $C_{15}H_{16}O_5$.
C,	65·28	65·21
H,	5·80	5·79

The following is a list of the acids and their anhydrides discussed in this and the preceding paper:

Melting Point.	Acid.	Anhydride.	Melting Point.
·139°	 $C_{10}H_4\begin{cases}O_2\\CH=CH-C_3H_7\\OH\end{cases}$ Lapachic Acid.		
·125°	 $C_{10}H_4\begin{cases}O_2\\CH_2-CH(OH)-C_3H_7\\OH\end{cases}$ Oxyhydrolapachic Acid.	 $C_{10}H_4\begin{cases}O_2\\CH_2-CH.C_3H_7\\O\underline{\hspace{3em}}/\end{cases}$ Lapachone.	155–6°
181–2°	 $C_{10}H_4\begin{cases}O_2\\CH(OH).CH(OH).C_3H_7\\OH\end{cases}$ Dioxyhydrolapachic Acid.	 $C_{10}H_4\begin{cases}O_2\\CH(OH).CH.C_3H_7\\O\underline{\hspace{3em}}/\end{cases}$ Oxylapachone.	201°
	Unknown.	 $C_{10}H_4\begin{cases}O_2\\CHBr-CH.C_3H_7\\O\underline{\hspace{3em}}/\end{cases}$ Bromlapachone.	138°

The acids are bright yellow in color, the anhydrides are orange or red. This distinction in color extends to other lapachic acid and lapachone derivatives which the author has obtained, but which have not yet been sufficiently studied to justify their introduction here.

NOTE ON THE COMPOUND OF PYRROL WITH PICRIC ACID.

By Samuel C. Hooker.

[*Read before the Chemical Section, February 18, 1890*].

In a short paper, devoted to some similar reactions of carbazol and pyrrol,* the author described, nearly two years ago, a compound which he had obtained from pyrrol and picric acid, fusing at about 71° and crystallizing in long red needles. The method of formation, as well as the properties of this compound, justified the assumption that it was an addition-product similar to the picric acid compounds of indol and carbazol.

Owing to the great instability of the compound, its analysis promised considerable difficulty, and was consequently deferred until the required leisure would make it possible to devote to it the necessary time and care.

By following the directions here given, no difficulty will be found in preparing the compound in a pure form: Freshly-distilled pyrrol is added to a small quantity of picric acid, in quantity a little more than may be necessary to cover it. As soon as the pyrrol comes in contact with the acid, the latter becomes intensely red. The temperature, which must at no time exceed 58°, is then gradually raised until the picric acid is completely dissolved. The heating must not be continued longer than is actually necessary for the picric acid to pass into solution. A short time after the temperature has fallen the compound separates in red needles, some long, others short and broad.

If a sufficient quantity of pyrrol be used in proportion to the picric acid and care be taken to heat as short a time as possible, the crystals are very easily freed from the mother liquor by pressure between filter paper. If, on the other hand, these points are not attended to, the mother liquor is so thick and sticky that simple pressure does not suffice to leave the crystals in a pure condition.

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* This *Journal*, **127**, 63.

To prepare the substance for analysis the mother liquor was drained off and the crystals were then rapidly and repeatedly pressed between porous paper until the paper was scarcely, or not at all, stained. The substance was then placed between well-fitting watch-glasses and immediately weighed. As soon as the crystals are dry, they commence to decompose, giving off pyrrol; they were, therefore, simply exposed to the air after the first weighing and then weighed again until the weight remained constant. The loss in weight represented the pyrrol given off, the residue consisted of picric acid.

(I) ·3230 gram lost ·0740 gram.
(II) ·5350 " " ·1210 "
(III) ·4460 " " ·1015 "

	Found.			*Calculated for*
	I.	*II.*	*III.*	$C_4H_5N, C_6H_3N_3O_7$
Pyrrol, ...	22·91	22·61	22·75	22·63
Picric acid, ...	77·09	77·39	77·25	77·37

That pyrrol was really given off from the crystal was ascertained by holding a pine splinter, moistened with hydrochloric acid, in the neighborhood of crystals which had been exposed for two or three hours (presumed to have been sufficiently long to have allowed all possible traces of pyrrol simply adhering to the crystals to have escaped); the characteristic reaction was obtained.

The residue was of a very pale yellow color, and fused, at the same time darkening, at about 120°. It dissolved almost entirely in water, leaving a minute quantity of a dark resin. Crystallized once from water it fused* at 120°–121°. The properties of the residue—its fusing point, the intense color and intensely bitter taste of its solution, its crystalline habits, etc.—corresponded exactly with those of picric acid.

Alcoholic solutions of pyrrol and picric acid deposit red crystals of the addition compound on spontaneous evaporation. The same is true of a chloroform solution. The combination does not appear to take place when benzol is the solvent employed.[*] Considering the very unstable nature of the pyrrol compound, it is not difficult to understand how the slight affinity, which exists between pyrrol and picric acid, may be overcome in the presence of relatively large quantities of benzol which itself forms an unstable compound with picric acid.

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* The fusing point of picric acid is 122°·5.

REPORT OF THE CHEMICAL SECTION OF THE FRANKLIN INSTITUTE FOR THE YEAR 1890.

Mr. Joseph M. Wilson, president Franklin Institute.

SIR :—I have the honor to submit the following report of the proceedings of the Chemical Section, for the year 1890.

The progress of the section during the year has been highly gratifying to its members, and while the report for 1889 showed for that period a condition of prosperity unprecedented in the history of the section, it is none the less true that the past year has entirely fulfilled the sanguine expectations of its members and all others interested in its progress and welfare.

The work of the section was prosecuted with the aid of the following officers:

President,	MR. T. C. PALMER.
Vice-presidents,	DR. H. F. KELLER, MR. W. L. ROWLAND.
Secretary,	DR. WM. C. DAY.
Treasurer,	DR. H. W. JAYNE.
Conservator,	DR. WM. H. WAHL.

Stated meetings were held, as required by the by-laws of the section, on the third Tuesday of each month of the year, excepting July and August.

Membership.—The number of members according to the treasurer's books, at the beginning of the year, was seventy-one; the number at present enrolled is seventy-two, three new members having been elected, while two have resigned.

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[*] M. Dennstedt, *Ber. d. chem. Ges.*, **21,** 34, 31.

Finances.—The report of the treasurer, submitted to the section at its last meeting, shows total receipts from various sources during the year amounting to	$138 00	
Cash on hand at beginning of the year, ...	91 50	
		$229 50
Disbursements amounted to		132 17
thus leaving a cash balance of . . . . in the hands of the treasurer at the end of the year.		$97 33

Attendance at meetings.—The meetings have been well attended by the members, and in almost every case the presence of a number of visitors has served to indicate the interest taken in the section by its outside friends.

Journals received by the section.—Early in the year the library committee authorized the purchase for the section of a complete set of *Liebig's Annalen* from 1832 to 1886. Subscription for this journal, beginning with 1887, was made by the section; this periodical, so essential as an auxiliary to scientific investigation, is therefore now complete.

Owing to the very satisfactory condition of the section's treasury, it has been found practicable during the year to add to the list of journals previously taken by the section the following, which are at present regularly received, viz: *Chemisches Centralblatt, Liebig's Annalen der Chemie, Zeitschrift für physiologische Chemie, Zeitschrift für Krystallographie, Tschermak's mineralogische Mittheilungen, Búlletin de la Société Chimique, Gazzetta Chimica Italiana.*

That the influence of the chemical section is making itself felt not only in Philadelphia and neighboring cities, but throughout the country, follows from the expressions of interest which in one way or another have frequently come to the notice of its members. Papers from writers in distant cities have been forwarded for consideration by the section and subsequent publication in the *Journal.*

Applications for membership from persons at a distance have also been made.

In view of these facts, the section has, at a recent meeting, appointed a committee for the purpose of considering means by which the attention of chemists at large may be called to the facilities for prompt publication which the institute possesses.

During the year sixteen important papers, giving the results of original investigation, have been read before the section. Nine communications of a miscellaneous character have been presented; thus making in all twenty-five matters of scientific interest which have occupied the attention of the section.

Very respectfully submitted,

Wm. C. Day,
Secretary.

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